

Hydro Chemical Assessment of Edipsos Geothermal Area, Greece

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Abstract. A geochemical survey on the thermal fluids of Edipsos area was undertaken. In order to investigate the *mineralization* process, a geochemical and isotopic analysis (major ions, ¹⁸O, ²H) was conducted for thermal waters of springs *and* boreholes. The Edipsos area is found in the north part of Euboea, south-east of Athens, and is characterized by high salinity waters. The evaluation of the geochemical data of the thermal waters of Edipsos suggests that they are fed by thermal water mixed with local groundwater and seawater. The most adequate geothermometers were applied on selected samples for the determination of the deep aquifer temperature.

1. Introduction

The thermal springs of Edipsos located in North Euboea are well known since ancient times as “Pausanias”, and were reported by Aristotle and others for their healing attributes. Despite that these springs were known from antiquity, the origin of the thermal water remains poorly documented. Dotsika [1] compared different geothermometers to assess the temperature of reservoirs concluded that Edipsos thermal field are high-enthalpy hydrothermal system.

2. Geology

The geology of northern Euboea (Figure 1) includes at the lower series a Permian–Triassic volcanoclastic complex. Its basement consists of metamorphic rocks of pre-middle to middle Carboniferous age, which are overlain by shallow marine clastic and carbonate rocks of middle Triassic age [2, 3]. The sedimentary rocks are intercalated with volcanic rocks that are overlain by Jurassic limestones. An ophiolitic corps, Late Jurassic–Early Cretaceous, is found above the limestones [2]. The volcanic rocks are best developed at the southeast part of Edipsos. The lithology is bedded tuff, fine grained agglomerate and rare ignimbrite. Fluvio-lacustrine deposits (Lower Miocene to Upper Pliocene) were formed during the earlier neotectonic phases of the region [4, 5].

The grabben of north Euboic gulf was formed during the last geological periods by NW–SE to WNW–ESE normal fault zones (Mettos et al. 1992). 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. 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. In Edipsos, thermogenic travertine deposits exist created by the local hot-springs.

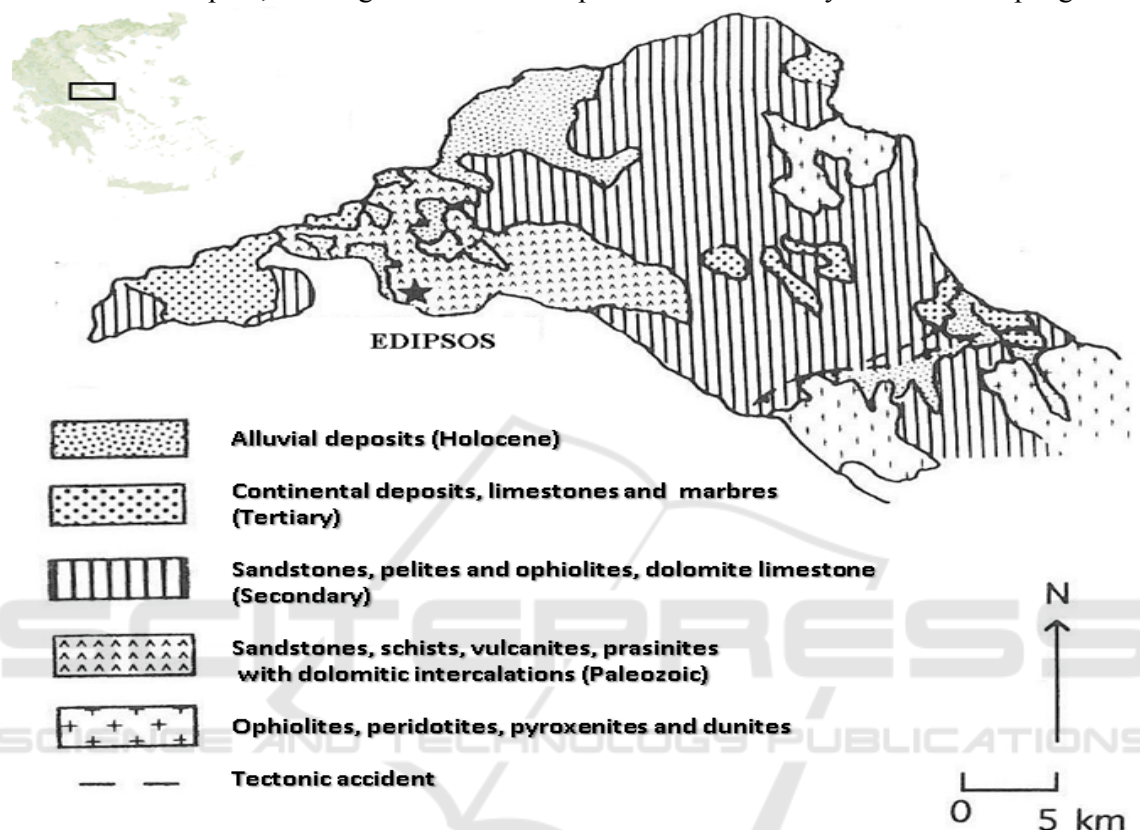


Figure 1. Simplified geological map of Edipsos area, according to the geological map of I.G.M.E. (1983).

3. Sampling and analysis

Sampling of waters was carried out in the Edipsos area. Thermal (a1,a2,a3,a4,a5,a6) and cold water were sampled with cold waters temperature ranging from 14.7 °C to 18 °C and thermal waters temperature ranging from 29.1 to 83°C. Temperature, pH, conductivity and alkalinity were measured directly in the field. Filtered (0.45 µm), acidified (with HNO₃ 1:1) water samples were collected for determination of cations and SiO₂. Untreated samples were collected for analyses of anions. The major chemical constituents were analysed according to the standard methods. Na⁺, K⁺, Ca²⁺, Mg²⁺ and SiO₂ contents were determined by atomic absorption. Anions were analysed by ion chromatography. The B⁺ content was determined photometrically using the curcumin method (Hayes and Metcalfé 1962). Chemical analyses were conducted at the Institute of Geosciences and Earth Resource, C.N.R., Pisa. The isotopic composition of the waters was conducted according to the isotopic methods for the ¹⁸O [6] and ²H analysis [7]. The results are expressed in delta (δ) ‰ vs SMOW (Standard Mean Ocean Water). The error for δ¹⁸O is ± 0.2 ‰ and for δ²H ± 2‰. Isotopic analyses were carried out at the Stable Isotopes Unit, N.C.S.R. “Demokritos”.

4. Hydrochemical and isotopic characteristics of the waters

In the studied area two prevalent water types are presented: Ca-HCO₃ and Na-Cl groundwater (Figure2). The group of water chemical type Ca-HCO₃ is comprised by cold waters. This chemical type usually refers to meteoric origin which also is confirmed by concentrations of TDS that range from 307.2 mg/L to 464.6 mg/L, less than 1000 mg/L, belonging to fresh water.

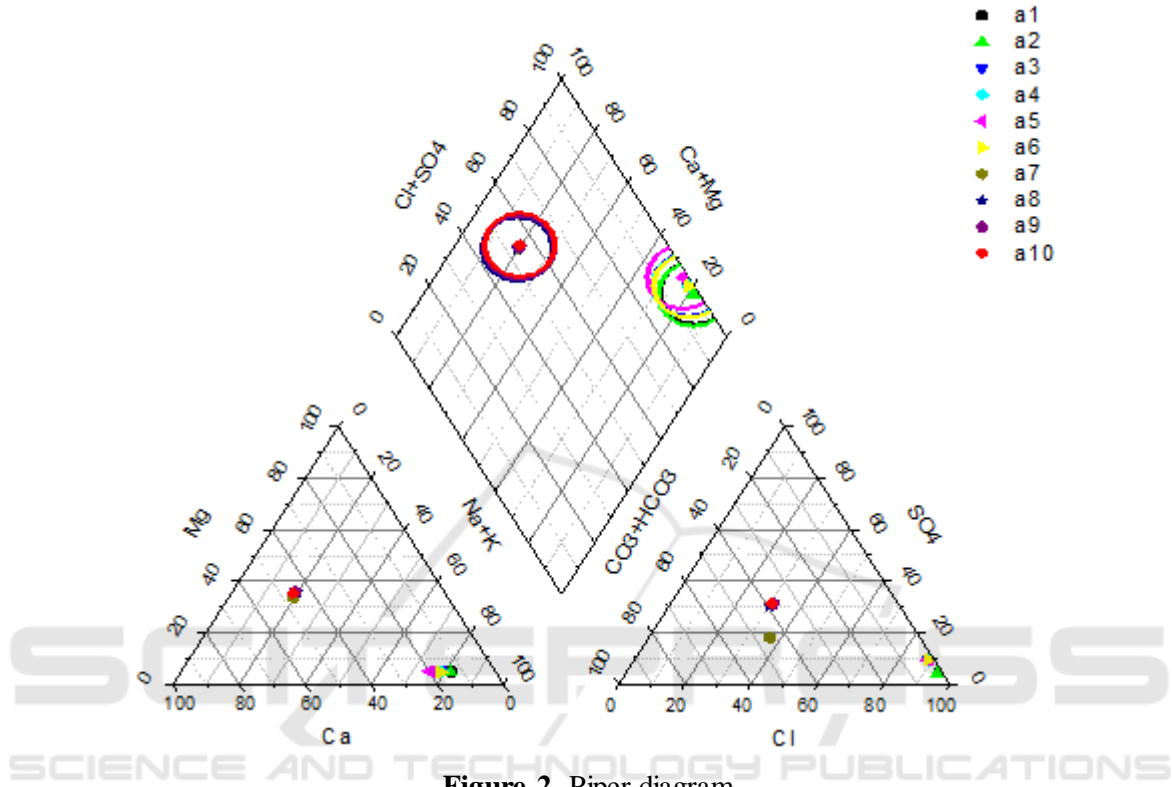


Figure 2. Piper diagram.

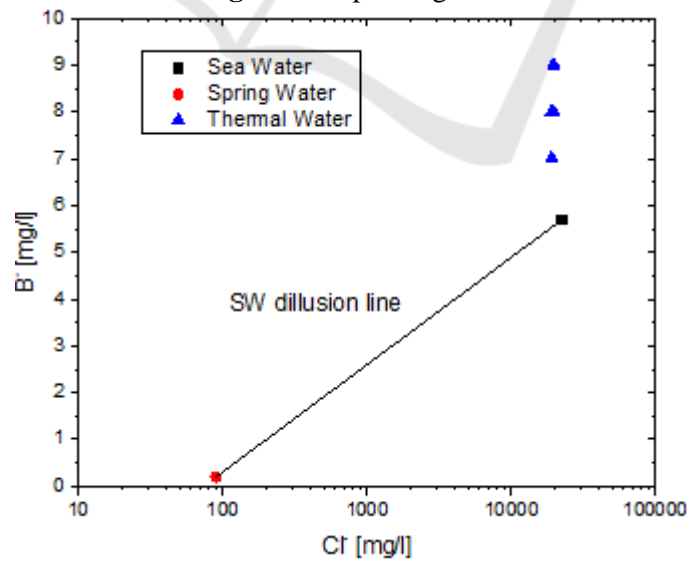


Figure 3. Graph of B⁺ versus Cl for cold and thermal waters of Edipsos.

The Na-Cl group includes the thermal springs and well together with the seawater. Their temperature ranges from 29.1 to 83°C with pH values indicating a slightly acid environment, (from 5.8 to 7.2). The thermal waters of Edipsos exhibit high values of B and Li in relation to sea water. The high concentration of B and Li can be explained by water-rock interactions processes. In order to clarify the mechanism of water-rock interaction B⁺ concentrations were plotted with respect to Cl⁻ (Figure 3) as they constitute conserved elements [8]. In this diagram we observe that the excess of B is not associated with a relevant excess in Cl in respect to seawater (the chlorine values remain stable).

Independent confirmation of the B⁺ transfer from the rock to the thermal waters may be possible to obtain through Li⁺, another conservative species also derived from the rock. Although B⁺ should be rather easily removed from sediments, the transfer of Li⁺ from rock requires intense water-rock interaction at high temperatures. Edipsos present also notable Li⁺ contents. The concentration of Li⁺ and B of thermal waters ranges from 1 to 1.6 mg/l and from 7 to 9 mg/l respectively. The high Li/B ratio of these waters also exhibits wide variability from 0.14 to 0.18 respectively, typical of water discharged 'arc-type' systems [9].

Apart from the water-rock interaction process that controls the Li⁺ and B⁺ contents, the Na⁺, Br⁻, Cl⁻ and most of SO₄²⁻ in thermal spring waters derive from sea water, which are more or less diluted by fresh, bicarbonate water and the supply of these ions by rock leaching is negligible. In fact the positive correlation between Cl⁻ and Na⁺ (and K⁺) indicates that high Cl⁻ contents of thermal waters arise from the contribution of seawater and/or a sodium-chloride geothermal liquid. But Bromine, in contrast to Na⁺, is considered to be conservative ion, even in geothermal environments, because its contents are not affected by interactions with rocks [10]. The Cl/Br ratio ranges from 283 to 340 values close to that of seawater. Assuming that chlorides in these samples have marine origin, we calculated that sea water at Edipsos seems to be involved in rate of 90-94%. Moreover, the thermal spring waters exhibit not only Br/Cl lower but also higher B/Cl and Li/Cl ratios than those of seawater, as stated above, indicating that the high-salinity end member cannot be actual marine water. It could be either marine water modified through water-rock interaction at high (or relatively high) temperature or a seawater-magmatic water mixture.

The isotopic values of the region's waters are plotted in the diagram of Figure 4 with the Global Meteoric Water Line [11] and the Eastern Mediterranean Water Line [12, 13]. The isotopic data of Edipsos thermal waters exhibit δ¹⁸O values similar to that of seawater, but differing δ²H. In particular, the δ¹⁸O values of Edipsos samples (δ¹⁸O values from -0.2‰ to 1‰) are close to that of seawater (δ¹⁸O ≈ 1‰) reflecting a seawater origin. However, this doesn't seem to apply for δ²H values which range from -11.7‰ to -3‰ (δ²H ≈ 6‰ for seawater). This observed vertical distribution of δ²H values suggests the above explanation (participation of magmatic water in the deep geothermal aquifer).

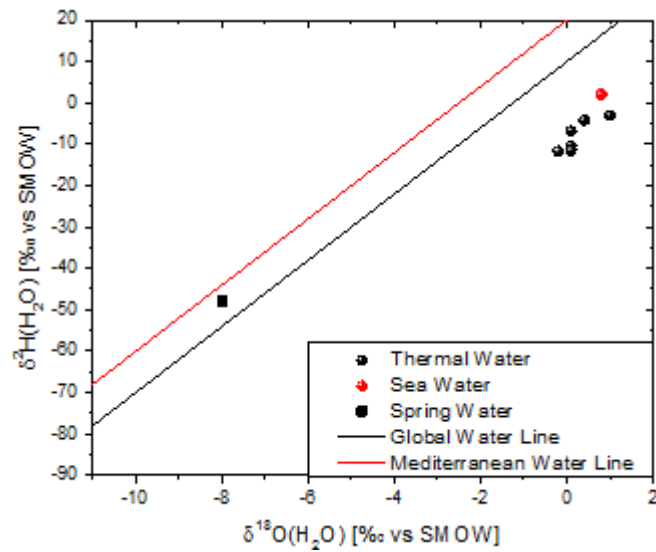


Figure 4. Diagram $\delta^{18}\text{O}$ vs $\delta^2\text{H}$.

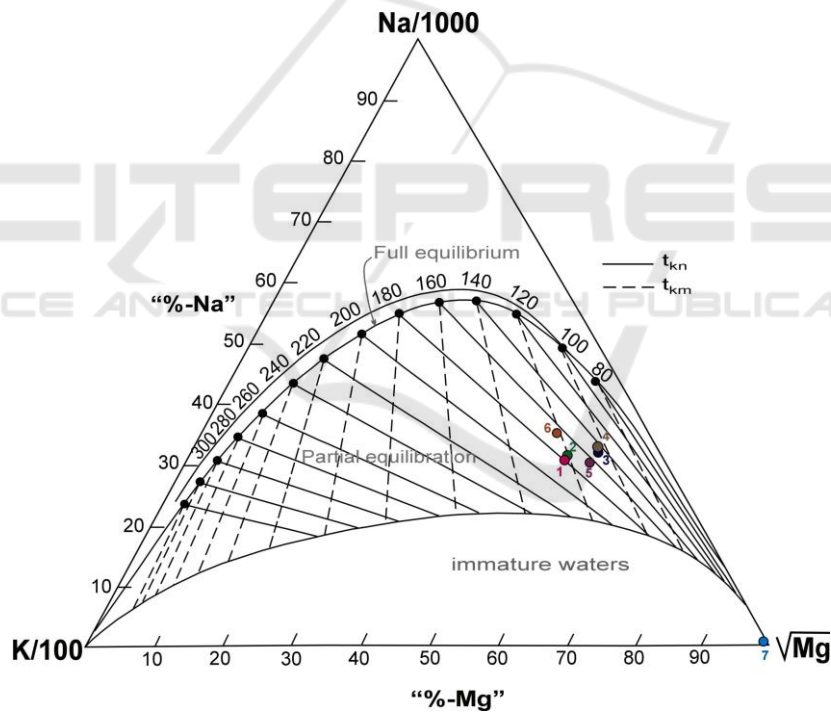


Figure 5. Giggenbach diagram.

^{34}S contents of the samples are compared to those of marine sulfate, which is very constant over the world ($\delta^{34}\text{S} = 20\text{‰}$ CD and $\delta^{18}\text{O} = 9.5\text{‰}$ SMOW; [14]). All the samples present $\delta^{34}\text{S}$ similar to that of seawater (20.5 to 19.4‰) but the $\delta^{18}\text{O}$ of the thermal spring water is very diminished in relation (6.8 to 7.2‰) to that of seawater. All the samples presented identical values of $\delta^{34}\text{S}-(\text{SO}_4)$ with respect to the value of seawater ($20\text{‰} \pm 1\text{‰}$ $\delta^{34}\text{S}$) while they were differentiated with respect to $\delta^{18}\text{O}-(\text{H}_2\text{O})$. The diminished $\delta^{18}\text{O}$ value of the SO_4^{2-} in the water of the springs in comparison to the

one of the SO_4^{4-} of sea water origin ($9.5 \pm 0.2\%$) could be attributed to isotopic equilibration between $\delta^{18}\text{O}-(\text{H}_2\text{O})$ and $\delta^{18}\text{O}-(\text{SO}_4)$.

5. Geothermometres

Geothermometres also contribute to the estimation of the subsurface reservoir temperatures in geothermal system (Table 1, fig 5). The operating principle of geothermometers is the representation of equilibrium of temperature-dependent reactions between minerals and the circulating fluids (for eg. [15]). Different geothermometers, chemical and isotopic, were applied to the thermal waters of Edipsos (Table 1). The isotopic geothermometer, ($^{18}\text{O}(\text{SO}_4^{2-} - \text{H}_2\text{O})$), that we use is based on the equilibrium exchange of oxygen isotopes between aqueous sulfate and water [16].

The resulting temperature is different for each chemical geothermometer with moderate to large variation. A possible cause could be sea water contribution, that possible disturbs the water – mineral equilibrium that the chemical geothermometers rely on. Furthermore, the only chemical geothermometer which would not be affected by the marine contribution is the quartz geothermometer that suggests a lower temperature. Regarding the isotopic geothermometers, if the $\delta^{18}\text{O}$ content of aqueous sulfate is only controlled by equilibration with water, and if isotopic equilibrium is reached (as the isotope of sulfate demonstrated), the temperature of geothermal fluid would be close to 234 °C.

Table 1. Temperatures (°C) calculated using different Geothermometer.

EDIPSOS	$^{18}\text{O}(\text{SO}_4^{2-}-\text{H}_2\text{O})$ [16]	Quarz (no steam loss) [17]	Na-K [18]	Na-K [15]	Na-K-Ca (TNKC) t°C (t>100°C) [15]
a1	230	104,3	147,54	127,56	147,25
a2	235	105,0	143,28	123,15	144,18
a3	230	100,6	162,12	142,72	157,16
a4	230	104,3	163,70	144,36	163,61
a5	-	-	131,05	110,52	83,69

6. Conclusions

The high B and Li^+ contents measured in these thermal waters show that the supply of these ions by rock leaching is significant. Especially the transfer of Li^+ from rock requires intense water-rock interaction at high temperatures. The use of isotopic geothermometer attributes a temperature greater than 200°C to the deep geothermal field.

References

- [1] Dotsika E 1991 *Utilisation du geothermometre isotopique sulfate-eau en milieux de haute temperature sous influence marine potentielle: Les systemes geothermaux de Grece* Thesis Paris 11
- [2] Katsikatsos G and et al 1986 *Geological structure of internal Hellenides (E. Thessaly–SW Macedonia–Euboea–Attica–Northern Cyclades islands and Lesvos)* Geological and Geophysical Research, Special Issue p 191-212
- [3] Katsikatsos G, M Vidakis and G Migiros 1981 *Platycampos sheet, Geological map of Greece 1: 50,000* Athens IGME
- [4] Guernet C 1971 *Études géologiques en Eubée et dans les régions voisines:(Grèce)* 91 résidence Bois des Godeaux
- [5] Ioakim C and et al 1992 *Evolution geodynamique et reconstruction paleoenvironnementale des bassins neogènes-quatérnaires de la Grèce centrale.* Paleontologia I evolució (24): p 393-

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- [6] Epstein S and T M 1953 *Variation of ^{18}O content of water from natural sources* Geochim. Cosmochim Acta 4: p 213–224
- [7] Coleman M L and et al 1982 *Reduction of water with zinc for hydrogen isotope analysis.* Analytical chemistry 54(6): p 993-995
- [8] Giggenbach W 1992 *Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin* Earth and planetary science letters 113(4): p 495-510
- [9] Giggenbach W and et al 1995 *Isotopic and chemical composition of waters and gases from the East Coast accretionary prism, New Zealand*
- [10] Henley R W and Ellis A J 1983 *Geothermal systems ancient and modern: a geochemical review* Earth-science reviews 19(1): p 1-50
- [11] Craig H 1961 *Isotopic variations in meteoric waters.* Science 133(3465): p 1702-1703
- [12] Aouad A and et al 2004 *Etude isotopique de la pluie et de la neige sur le Mont Liban: premiers résultats/Isotope study of snow and rain on Mount Lebanon: preliminary results* Hydrological Sciences Journal 49(3)
- [13] Bowen G J and Wilkinson B 2002 *Spatial distribution of $\delta^{18}O$ in meteoric precipitation* Geology 30(4): p 315-318
- [14] Longinelli A 1989 *Oxygen-18 and sulphur-34 in dissolved oceanic sulphate and phosphate the marine environment* p 219-255
- [15] Fournier R and Truesdell A 1973 *An empirical Na-K-Cageothermometer for natural waters* Geochimica et Cosmochimica Acta 37(5): p 1255-1275
- [16] Lloyd R 1968 *Oxygen isotope behavior in the sulfate - water system.* Journal of Geophysical Research 73(18): p 6099-6110
- [17] Fournier R 1977 *Chemical geothermometers and mixing models for geothermal systems.* Geothermics 5(1-4): p 41-50
- [18] Giggenbach W F 1988 *Geothermal solute equilibria. derivation of Na-K-Mg-Ca geoindicators.* Geochimica et cosmochimica acta 52(12): p 2749-2765