

# Chemical And Isotopic Characterization Of The Thermal Fluids In The South-western Margin of the Loutros-Feres-Soufli Tertiary Basin in Northern Greece. Case Study: Geothermal Area of Aristino

DALAMPAKIS P.<sup>1</sup>, SPYRIDONOS E.<sup>2</sup>, TASSI M.<sup>3,\*</sup>, KARALIS P.<sup>3</sup>, DOTSIKA E.<sup>3,4</sup> and PAGONIS G.<sup>3</sup>

<sup>1</sup>Hellenic Agricultural Organization – DEMETER, Soil and Water Resources Institute - Sindos

<sup>2</sup>PPC Renewables S.A., 15341 Ag. Paraskevi Attikis, Greece

<sup>3</sup>Stable Isotope Unit, N.C.S.R. “Demokritos”, 15310 Ag. Paraskevi Attikis, Greece

<sup>4</sup>Institute of Geosciences and Earth Resources, C.N.R., Via G. Moruzzi 1, 56124 Pisa, Italy

\*corresponding author:

e-mail: m.tassi@inn.demokritos.gr

**Abstract** In this work we examine the hydrochemical and isotopic characteristics of the thermal fluids in the Aristino geothermal area in the southwestern margin of the Loutros-Feres-Soufli Tertiary basin (LFS), which is located west of Evros river in Northeastern Greece, in order to identify their possible origin and the expected procedures responsible for the alteration of the initial composition of them. The studied fluids are characterized by high  $\text{Cl}^-$  and  $\text{Br}^-$  contents, which indicate a higher or lower marine contribution. Furthermore, the elevated B and  $\text{Li}^+$  values and the low  $\text{Mg}^{2+}$  values respectively, are related to high temperatures indicative of water-rock interaction procedures. Additionally, we observe an enrichment of  $\delta^{18}\text{O}$  values, which is another indicator of water-rock interaction that occurs in areas with high thermal potential. Finally, we attempt to evaluate the deep reservoir temperatures with the application geothermometers. Their values reflect an equilibrium process with the probable existence of a deep hydrothermal system of middle to high enthalpy.

**Keywords:** geothermal system, water geochemistry, O-H isotopes, geothermometry

## 1. Introduction

The isotope analysis of geothermal fluids can provide information about the recharge areas, their origin, the water rock interaction, the temperature of reservoirs and the flow patterns. Furthermore, the study of chemical and isotopic fingerprint, such as major elements, Li, B,  $^{34}\text{S}$ ,  $^{13}\text{C}$ ,  $^{18}\text{O}$ ,  $^2\text{H}$ ,) (Dotsika, 2012, Dotsika, 2015), can shed light on the mixing processes that occur between sea water, magmatic and meteoric water. Hence, these hydrochemical chemical isotopic measurements are very essential in order to reconstruct the hydrochemical model of a geothermal field. Two distinct geothermal areas were recognized in the LFS basin during a long-standing exploration period since 1988. Production wells in the Fylakto-Tychero geothermal area, which is located in the northern part of the LFS basin, has revealed the presence

of rich aquifers with Na-Cl type geothermal waters (Dotsika et al., 1997) with maximum temperature of  $37^\circ\text{C}$  and minimum flow rate at  $250 \text{ m}^3/\text{h}$ . The most promising geothermal field in the LFS basin has been investigated and confirmed in the Aristino area 10 Km east of Alexandroupolis. Over 15 production and exploratory wells have revealed the presence of a fault controlled hydrothermal system with two distinct overlapping hot aquifers at depths ranging between 200 and 400 m. Water temperature as high as  $99^\circ\text{C}$  was measured during production tests. In this work we evaluated chemical ( $\text{Cl}^-$ ,  $\text{Br}^-$ , B,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ) and isotope ( $^{18}\text{O}$ ,  $^2\text{H}$ ) analysis for fluids sampled from boreholes drilled in the Aristino geothermal field and we have proceeded to the evaluation of the expected reservoir temperatures via isotopic geothermometers.

### 1.1. The Loutros-Feres-Soufli basin

The Loutros-Feres-Soufli basin (LFS) is located west of the Evros river and is one of the three subdepocentres of the Evros Delta Tertiary basin, including the oldest sedimentary section of Southern Rhodopes (Caracciolo, et al., 2015). According Kolios et al., 2007 the stratigraphic succession of the basin can be summarized as following: The Paleogene – Eocene sediments have been deposited unconformably upon the Mesozoic formations or to the west upon the gneisses, amphibolites and ophiolites of the Rhodope massif. The marine Paleogene sediments (average thickness of about 2000 m) consist of sandstones, marls, limestones, polygenic volcanic breccias, tuffs and siltstones. The Neogene and Quaternary sediments (maximum thickness of 1500 m) consist of clays, siltstones, sandstones, lignite layers and in the upper section of the sedimentary sequence sands, sandstones and clays exist. The beginning of the marine Tertiary transgression in the Evros basin is suggested during the Middle Eocene (Lutetian).

An intense volcanic activity has occurred during Eocene and Oligocene, culminated at the Late Oligocene. Volcanic products of the basin consist of pyroclastics, interlayered with Oligocene sediments, rhyolitic

ignimbrites, lava flows, breccias, and domes and dykes. Volcanism ended in the Miocene with both acid and intermediate volcanic products (Eleftheriadis, et al., 1994) In Table 1 we present some characteristics of the Aristino wells.

**Table 1.** Characteristics of representative wells drilled in the Aristino geothermal field

| Sample Code                | Aquifer           | Reservoir roof (thickness) (m) | Formations                                    |
|----------------------------|-------------------|--------------------------------|---|
| AA1E<br>EB1                | Aristino<br>upper | 200 (20)<br>100-150 (20)       | Volcaniclastic<br>Altered dacitic<br>lavas    |
| KO1<br>EB3<br>AA1P<br>AA3P | Aristino<br>lower | 100-250 (30)<br>330-430 (30)   | Altered dacitic<br>lavas-tuffs<br>Ignimbrites |

## 2. Sampling and Methodology

The temperature was measured directly in the field, while for the chemical analyses, water samples were collected in polyethylene containers of 700ml. Additionally, for the isotope analysis of water ( $^{18}\text{O}$ ,  $^2\text{H}$ ), samples were taken separately in two-glass bottles (50ml and 1L) at every sampling point. For the boron content the water samples were acidified and evaporated to dryness (at 55 °C) in the presence of curcumin. The red precipitate dissolved in ethyl alcohol and the alcoholic mixture was photometrically measured at 540nm (Eaton, et al., 1995). The water samples were analyzed at the Institute of Geosciences and Earth Resource, C.N.R.-Pisa and IGME. The lithium was determined by inductively coupled plasma optical emission spectrometry with a precision of better than  $\pm 2\%$ . The isotopic composition of oxygen ( $\delta^{18}\text{O}$ ) and hydrogen ( $\delta^2\text{H}$ ) was measured at the Stable Isotope laboratory National Center for Scientific Research “Demokritos” and the ratios were determined in water samples using the  $\text{CO}_2\text{-H}_2\text{-water}$  equilibration method (Duhr and Hilkert, 2004, Hilkert and Avak, 2004).

The isotope composition of  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ , is indicated in delta notation, versus Vienna Standard Mean Ocean Water (VSMOW) as:

$$\delta = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] * 1000$$

where  $R_{\text{sample}}$  and  $R_{\text{standard}}$  are  $^2\text{H}/^1\text{H}$  or  $^{18}\text{O}/^{16}\text{O}$  ratios of samples and standard respectively. The measurement precision was  $\pm 1\text{‰}$  for  $\delta^2\text{H} \pm 0.1\text{‰}$  for  $\delta^{18}\text{O}$ .

## 3. Results

### 3.1 Hydrochemistry

The results of chemical analysis are shown in Table 2. The samples' temperature ranges from 31 to 93 °C and the  $\text{Cl}^-$  content is  $>2000$  mg/L except from EB-2. The  $\text{Cl}^-$  and  $\text{Br}^-$  are used for the identification of chlorine's origin, as these ions are conservative ones even in geothermal systems (Dotsika, 2012, Dotsika, 2015, Dotsika and Michelot, 1992, Dotsika, et al., 2009, Henley and Ellis, 1983, Michelot, et al., 1993), unlike  $\text{B}^+$ ,  $\text{Li}^+$  and  $^{18}\text{O}$ , which are affected by interactions with the rocks. Additionally, we observe that  $\text{B}^+$  ranges between 3.2 and

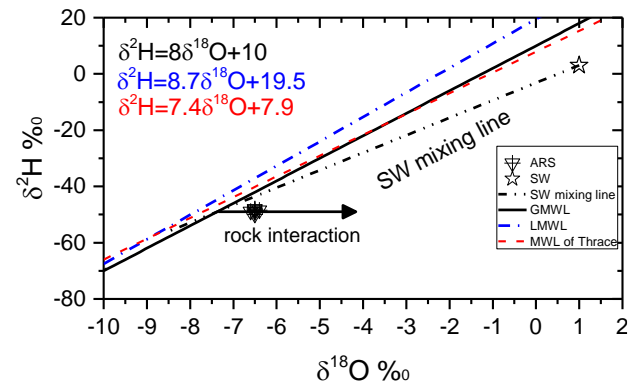
11.3 mg/L and thus the B/Cl ratio, is higher about 3 times than that of seawater which is an indicator that the excess of B can be of marine sedimentary origin. Furthermore, these samples are rich in  $\text{Li}^+$  and the ratio  $\text{Li}/\text{Cl}$  is 163 times greater than that of seawater.

**Table 2.** Temperature and chemical analysis results of geothermal water samples from the Aristino wells. ( $^1$ Poutoukis et al., 1998;  $^2$ Kolios, 2001)

| Sample             | T    | $\text{Cl}^-$ | $\text{Br}^-$ | $\text{Li}^+$ | $\text{B}^+$ |
|--------------------|------|---------------|---------------|---------------|--------------|
|                    | (°C) | (mg/L)        |               |               |              |
| KO1 <sup>1</sup>   | 78   | 4610.0        |               | 3.00          | 7.0          |
| EB1 <sup>1</sup>   | 43   | 145.0         |               |               | 3.2          |
| EB3 <sup>1</sup>   | 79   | 3748.0        |               |               | 5.7          |
| EB3-1 <sup>1</sup> | 85   | 2252.0        |               |               |              |
| EB3-2 <sup>1</sup> | 93   | 4960.0        |               | 6.90          | 7.0          |
| AA1E <sup>2</sup>  | 72   | 4255.2        | 17            | 7.00          | 7.0          |
| AA1P <sup>2</sup>  | 52   | 5283.5        |               | 6.90          | 6.5          |
| AA2 <sup>2</sup>   | 31   | 4982.1        |               | 7.80          | 11.3         |
| AA3 <sup>2</sup>   | 89   | 5655.9        |               | 7.10          | 7.0          |
| AA4 <sup>2</sup>   | 64   | 5212.6        |               | 7.00          | 8.8          |
| AA5 <sup>2</sup>   | 33   | 3840.0        |               |               | 9.0          |

### 3.2 Isotope analysis

The  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotope values range from -6.6 to -6.4 ‰ and -50.0 to -48.0 ‰ respectively. In Figure 1 we present the isotopic results versus Local Meteoric Water Line for Greece (Dotsika, et al., 2010), local Meteoric Water Line of Thrace (Dotsika, et al., 2018, Dotsika, et al., 2010), Global Meteoric Line (Craig, 1961) and Seawater Mixing Line



**Figure 1.**  $\delta^{18}\text{O}$  versus  $\delta^2\text{H}$  of the thermal waters for all studied areas. The black solid line is the Global Meteoric Water Line the blue dash-dot line is the Local Meteoric Water Line and the red dash line is the Meteoric Water Line of Thrace.

We observe that the oxygen isotopic values of our samples fall to the right of mixing point and below the Local Meteoric Line denoting that the significant oxygen isotope enrichment results not only from mixing water but also from isotopic exchange with the rocks. The horizontal line that begins from the mixing point and continues higher to  $\delta^{18}\text{O}$  values represents an ‘oxygen shift’ that is caused by water–rock interaction process. This positive oxygen shift, at least of 1.5 ‰, seems to occur in areas of high temperatures of the geothermal reservoir, a fact that is, also, supported by the high values

of  $\text{Li}^+$  and  $\text{B}^+$ , whose transfer from rocks requires water-rock interactions that occur at high temperatures.

### 3.3 Geothermometry

The reservoir temperature was estimated by the application of the following geothermometers:  $\text{SiO}_2$  (Fournier, 1981), Li–Mg (Kharaka and Mariner, 1989), Na–K (Arnorsson, 1983), Na–Li (Fouillac and Michard, 1981) and Na–K–Ca (Fournier and Truesdell, 1973). The temperatures estimated are different among the various geothermometers, due mainly to the marine contribution to the deep thermal fluids. Moreover, the  $\text{SiO}_2$  geothermometer temperature (70–130°C) which is not affected by the marine contribution does not agree with the maximum temperature of 170°C and 200°C estimated by the Na–K and Na–K–Ca geothermometers, respectively. Furthermore, the Na–Li (75–190°C) and Li–Mg (55–120°C) geothermometers also exhibit values much lower than those taken by the Na–K–Ca but similar to those of the  $\text{SiO}_2$  and Na–K geothermometers. In all, the temperature obtained using  $\text{SiO}_2$  geothermometer is considered the lowest one, attributable to the deep hydrothermal system. Thus, isotopic geothermometers values reflect an equilibrium process with the probable existence of a deep geothermal field of middle to high enthalpy.

## 4. Conclusions

In this work we evaluated chemical and isotopic analysis of geothermal waters from the Aristino geothermal field. We observed enrichment in  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $\text{Cl}^-$  which are indicators of seawater contribution in deep geothermal reservoirs. Furthermore, the oxygen isotopes values showed the ‘oxygen shift’ that represents a water-rock interaction process. Moreover, there is an increase to  $\text{Li}^+$  and  $\text{B}^+$  content, that is one more factor that shows an intense water-rock interaction at high temperatures. Additionally, chemical geothermometers were used for the estimation of reservoir temperature, and their results reflect an equilibrium process with the probable existence of a deep geothermal field of middle to high enthalpy.

## References

- Arnorsson, S., 1983. Chemical equilibria in Icelandic geothermal systems—implications for chemical geothermometry investigations, *Geothermics* 12, 119–128.
- Caracciolo, L., Orlando, A., Critelli, S., Kolios, N., Manetti, P., Marchev, P., 2015. The Tertiary Thrace basins of SE Bulgaria and NE Greece: a review of petrological and mineralogical data of sedimentary sequences, *Vulcanologica* 25, 21–41.
- Craig, H., 1961. Isotopic variations in meteoric waters, *Science* 133, 1702–1703.
- Dotsika, E., 2012. Isotope and hydrochemical assessment of the Samothraki Island geothermal area, Greece, *Journal of volcanology and geothermal research* 233, 18–26.
- Dotsika, E., 2015. H–O–C–S isotope and geochemical assessment of the geothermal area of Central Greece, *Journal of Geochemical Exploration* 150, 1–15.
- Dotsika, E., Diamantopoulos, G., Lykoudis, S., Poutoukis, D., Kranioti, E., 2018. Isotopic composition of spring water in Greece: spring waters isoscapes, *Geosciences* 8, 238.
- Dotsika, E., Lykoudis, S., Poutoukis, D., 2010. Spatial distribution of the isotopic composition of precipitation and spring water in Greece, *Global and Planetary Change* 71, 141–149.
- Dotsika, E., Michelot, J.-L., 1992. Origine et températures en profondeur des eaux thermales d'Ikaria (Grèce), *Comptes rendus de l'Académie des sciences. Série 2, Mécanique, Physique, Chimie, Sciences de l'univers, Sciences de la Terre* 315, 1261–1266.
- Dotsika, E., Poutoukis, D., Michelot, J., Raco, B., 2009. Natural tracers for identifying the origin of the thermal fluids emerging along the Aegean Volcanic arc (Greece): Evidence of Arc-Type Magmatic Water (ATMW) participation, *Journal of Volcanology and Geothermal Research* 179, 19–32.
- Duhr, A., Hilkert, A., 2004. Application note 30049: Automated  $\text{H}_2/\text{H}_2\text{O}$  equilibration for  $\delta\text{D}$  determination on aqueous samples using thermo scientific GasBench II, Bremen, Germany: Thermo Fisher Scientific.
- Eaton, A.D., Clesceri, L., Greenberg, A., 1995. Standard methods for the examination of water and wastewater: Washington, DC, American Public Health Association.
- Eleftheriadis, G., Pe-Piper, G., Christofides, G., Soldatos, T., Esson, J., 1994. K–Ar dating of the Samothraki volcanic rocks, Thrace, North-Eastern Aegean (Greece), *Bull. Geol. Soc. Greece* 30, 205–212.
- Fouillac, C., Michard, G., 1981. Sodium/lithium ratio in water applied to geothermometry of geothermal reservoirs, *Geothermics* 10, 55–70.
- Fournier, R., 1981. Application of water geochemistry to geothermal exploration and reservoir engineering, *Principles and Case Histories, Geothermal systems*, 109–143.

Fournier, R., Truesdell, A., 1973. An empirical Na-K-Ca geothermometer for natural waters, *Geochim Cosmochim Acta* 37, 1255-1275.

Henley, R.W., Ellis, A.J., 1983. Geothermal systems ancient and modern: a geochemical review, *Earth-science reviews* 19, 1-50.

Hilkert, A., Avak, H., 2004. Application note 30048: 18 O-equilibration on water, fruit juice and wine using thermo scientific GasBench II, Thermo Fisher Scientific, Bremen, Germany.

Kharaka, Y.K., Mariner, R.H., 1989. Chemical geothermometers and their application to formation waters from sedimentary basins, *Thermal history of sedimentary basins*, Springer, pp. 99-117.

Michelot, J.-L., Dotsika, E., Fytikas, M., 1993. A hydrochemical and isotopic study of thermal waters on Lesbos Island (Greece), *Geothermics* 22, 91-99.