

Geochemical Study of the Geothermal Field of Nigrita, Greece

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Abstract. In order to investigate the mineralisation process, we conducted geochemical and isotopic analyses (major ions, ¹⁸O, ²H) of the thermal waters of springs and boreholes of Nigrita. This study shows that the thermal waters are of meteoric origin. Appropriate geothermometers were applied on selected samples of thermal waters for the determination of the deep aquifer temperature.

1. Introduction

The thermal springs of Nigrita are located in North Greece. The geothermal anomaly manifests itself mainly by the intersection of the fault systems of the area. The main thermal reservoir is located at the basalt conglomerate containing water at a highest temperature of 600°C. Appropriate geothermometers were applied on selected samples of thermal waters for the determination of the deep aquifer temperature.

2. Geology

The geological background (Figure 1) of the area consists of metamorphic rocks of the Serbomacedonian mass and thick sedimentary deposits of Neogene age, which are rich in clay and marl components, and present poor hydraulic characteristics.

The aquifer body consists of a basal conglomerate formation which develops at the depth of 70 to 500 m. The reservoir presents pressurized heads, and measured temperatures range from 40 to 64°C.

3. Sampling and analytical methods

The water samples were collected from the area of Nigrita-Therma for isotopic analysis. For the chemical analyses, water was sampled in plastic bottles of 700ml. Two bottles of waters were taken for the chemical analyses, one acidized (HNO₃ 1:1), for cation analysis and one not-acidized for

anion analysis. Chemical analyses were conducted at the Institute of Geosciences and Earth Resource, C.N.R., Pisa. One glass bottle of water (50ml) was taken for the isotopic analyses (^{18}O and ^2H). In situ, conductivity, temperature, pH and bicarbonates were measured. For this purpose, several instruments were used, including digital pH-meter, control-solutions pH 4 and 7 for the calibration of the pH-meter, automatic digital conductometer for conductivity and temperature measurements, control-solutions for the calibration of the conductometer, dense nitric acid, HNO_3 65%, 1,40 Kg/l density, portable fridge for the storage of the samples.

The isotopic composition of the waters was conducted according to the isotopic method for the ^{18}O [1] and ^2H analysis [2]. The results of the stable isotope are expressed in delta (δ) ‰ vs SMOW (Standard Mean Ocean Water). The error for $\delta^{18}\text{O}$ is ± 0.2 ‰ and for $\delta^2\text{H}$ ± 2 ‰. Isotopic analyses were conducted at the Unit of Stable Isotopes, Institute of Nanoscience and Nanotechnology, N.C.S.R. "Demokritos" and at the Institute of Geosciences and Earth Resource, C.N.R., Pisa.

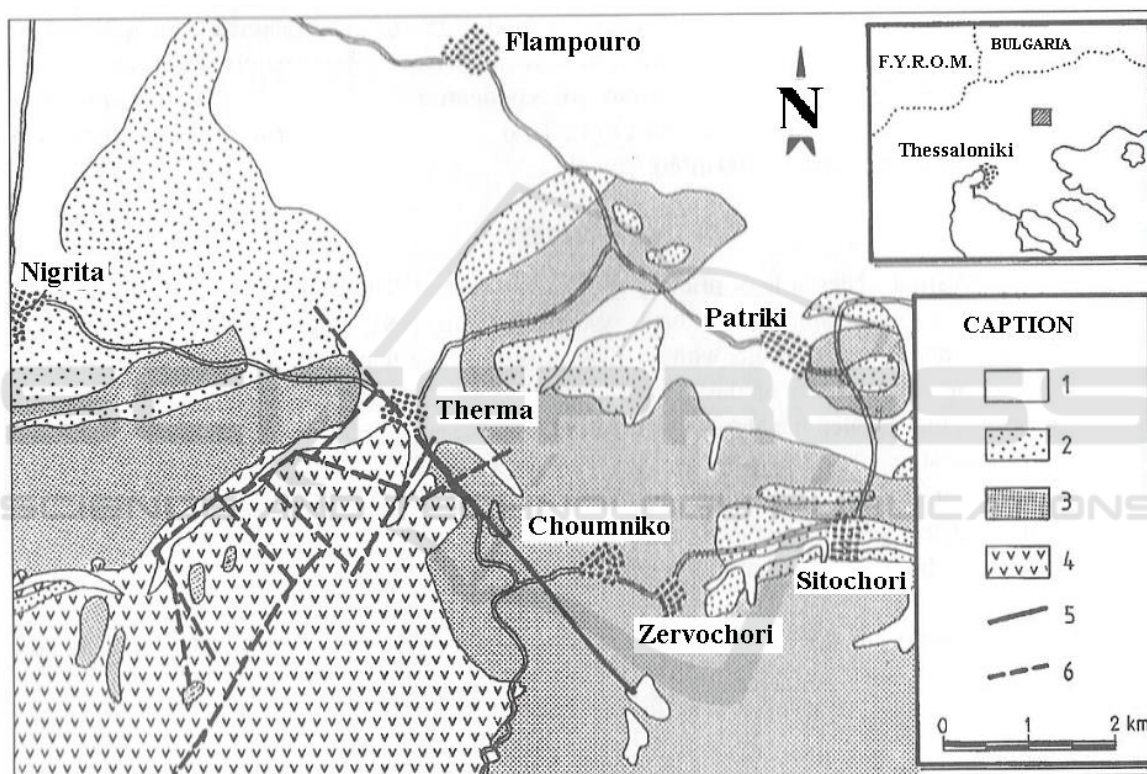


Figure 1. Simplified geological map of Therma-Nigrita area, on the basis of the geological map of I.G.M.E. [1. Sandy clays, sands, gravels, alluvial fans (Holocene), 2. Sands, gravels, clays, loams (Pleistocene), 3. Fine-layered silts, clays, sandy clays, lacustrine limestones, marls, sandy marls, marly limestones, silts, intercalations of gravel layers, sands, basal conglomerate (Neogene), 4. Ophiolites, 5. Faults, 6. Propable faults].

4. Hydrochemistry

9 samples of water were collected for this study: 3 cold waters from boreholes (samples N-4, N-6, N-8), 2 semi thermal water from borehole (N-5, N-9: 22 and 27°C respectively) and 4 from thermal springs (samples TH-1, TH-2, TH-3, TH-5). Bibliographic data were also considered [3]. The sampling was carried out between June 2013 and July 2015. The temperatures of borehole, waters varied between 17 and 27 °C, although the ambient temperature for the last 30 years averaged 17.5 °C. All the boreholes samples are of Ca- HCO_3 type (Figure 2).

In the Na versus Cl diagram (Figure 2) the samples follow a relation between the low TDS fresh cold borehole water with the thermal springs. This indicates the occurrences of mixing between a low Na-Cl component and a high Na-Cl component. The first is probably diluted ground water while the later maybe water of geothermal reservoir. The relatively low concentration of Cl^- in these waters excludes contamination of shallow aquifers with seawater. On the other hand, the possibility that some of the Na^+ and Cl^- ions contained in well waters come from marine spray cannot be excluded (Figure 3).

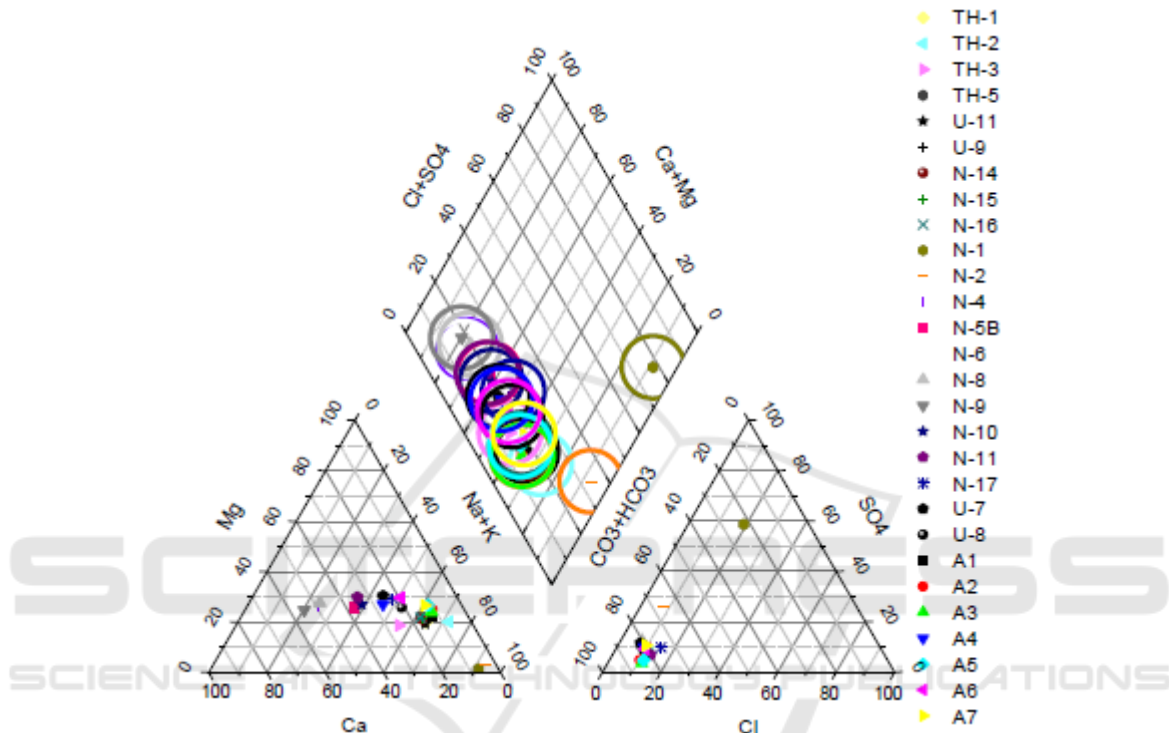


Figure 2. Chemical types of the waters.

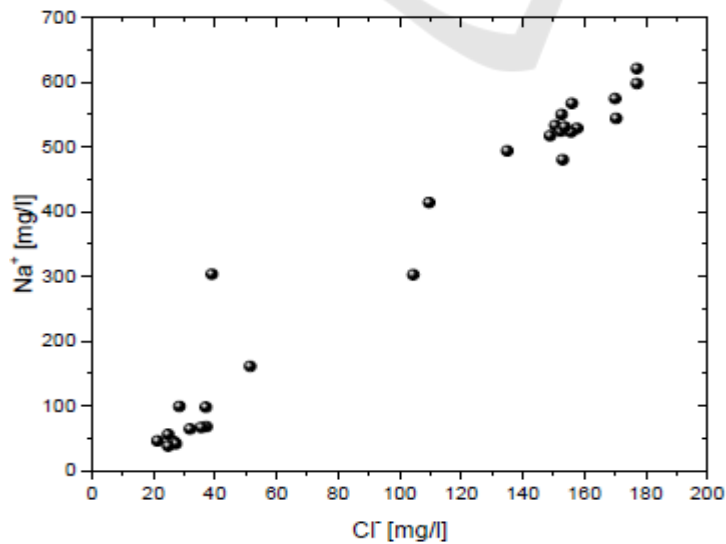


Figure 3. Na versus Cl contents.

These waters in general are superficial waters in their first stages of interaction with the rocks. In fact the TDS in the Ca-HCO₃ type waters from borehole is in the interval of 0.5 to 1.5g/L. The sampled thermal waters of this area are Na-HCO₃ type with high B contents (3 mg/L) showing that the supply of boron by rock leaching is significant. The relatively high HCO₃⁻, which is observed in the hot springs, relates with absorption of CO₂-bearing gases or with condensation of CO₂ geothermal steam. The waters, in which the condensation of the geothermal steam took place, have a high composition in bicarbonates (i.e. 1600-2300 mg/L) (Figure 4) and are found in the marginal zone of geothermal liquid-dominated systems. The differentiation of hot waters, rich in B and HCO₃ content from the others and the gradual increase of Cl⁻ content confirm that these waters are mixed with a deeper geothermal fluid.

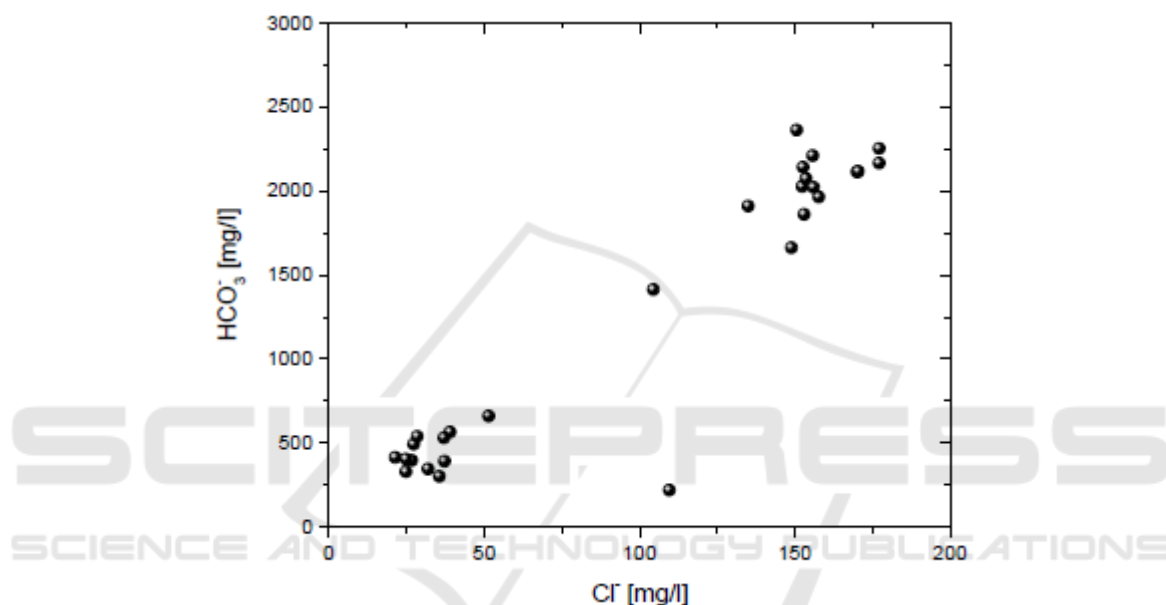


Figure 4. HCO₃ versus Cl contents.

5. Stable isotopes of water

Analyses of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ have been performed on all samples. The stable isotope contents of $\delta^{18}\text{O}$ ranging from -8.8 to -8.5‰ and $\delta^2\text{H}$ from -56 to -55.9‰ . The isotopic values of the region's waters are plotted in the diagram of Figure 4 along with the Global Meteoric Water Line and the Eastern Mediterranean Water Line. The cold and thermal waters are plotted between these two lines (Global: $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$, [4] and E. Mediterranean: $\delta^2\text{H} = 8\delta^{18}\text{O} + 22$, [5, 6]). In Figure 5 it is shown that the composition of the Nigrita waters is mainly meteoric, ruling out the isotopic exchange with the geological environment under temperature, evaporation or mixing with isotopically different waters.

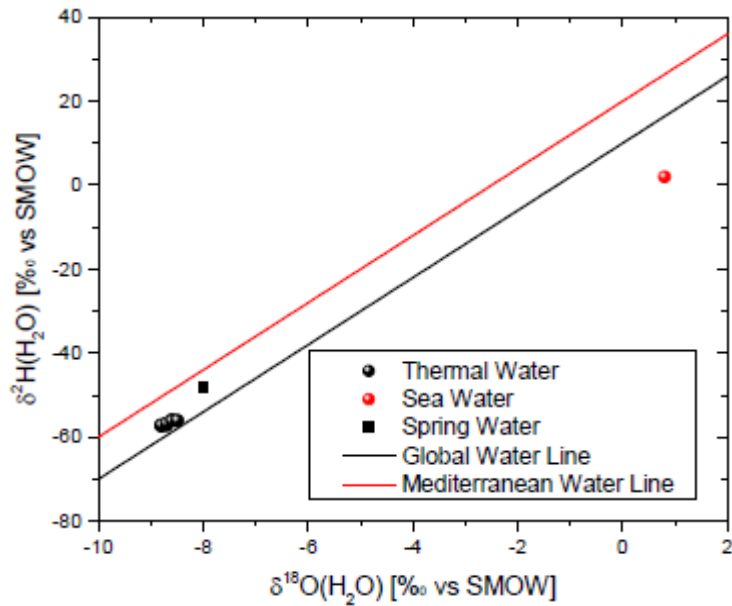


Figure 5. Diagram $\delta^{18}\text{O}$ vs $\delta^2\text{H}$.

6. Geothermometry of the waters

For the determination of the temperature of the deep geothermal fluids, the chemical geothermometers applied are SiO_2 [7], Na/K [8], Na-K-Ca [9], Na-Li [10], K-Mg [11] and Li-Mg [12] on the geothermal waters of Nigrita basin. The results of the application of these chemical geothermometers are reported in Table 1 and Figure 6.

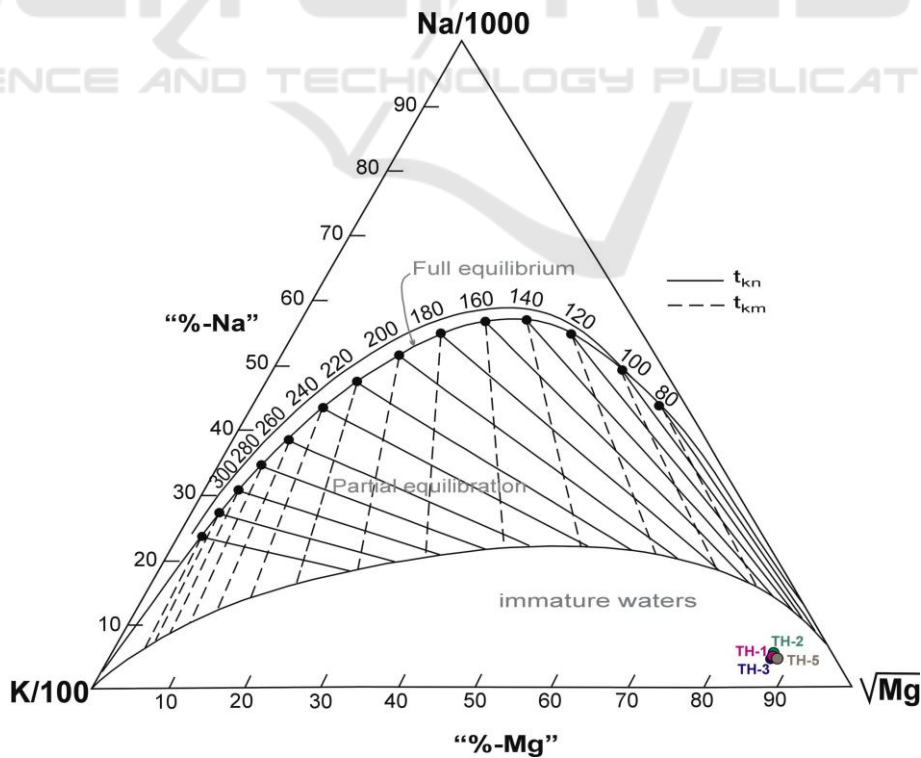


Figure 6. Giggenbach diagram.

The resulting temperatures are different for each geothermometer with moderate to large variation with the exception of the temperatures resulting from the Li-Mg geothermometer, which are almost identical to the measured temperatures of the emerging thermal waters. Probably the high temperatures of the other geothermometers, are due to the state of non-equilibrium of the water in the thermal reservoir as calculated by the saturation indexes (PHREEQC). Contrary, the waters are sursaturated in quartz [13] allowing the use of SiO₂ geothermometer. The temperature proposed is about 110 °C that we accept as the lowest for this geothermic system. These temperatures are close to that estimated (130-150° C) from [3] with the use of the isotopic geothermometer (sulfur isotopic geothermometer is based on the equilibration of $\delta^{18}\text{O}$ between SO₄²⁻-H₂O).

Table 1. Estimation of the temperature (°C) of the deep reservoir by the use of geothermometers for the geothermal waters of the Nigrita region.

	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)	T (°C)
	SiO ₂	Na/K	Na-K-Ca	Na-Li	K/Mg	Li-Mg
TH-1	118.9	244.7	210.5	138.3	91.5	76.3
TH-2	118.9	241.3	217.2		92.0	
TH-3	102.2	266.2	214.2	94.4	94.8	60.0
TH-5	107.0	257.4	215.9	97.0	92.0	60.2

7. Conclusions

The chemical data of the thermal water samples indicate the mixing between deep geothermal water and cold water. Furthermore, the high B contents measured in these thermal waters show that the supply of boron by rock leaching is significant. The use of chemical geothermometer attributes a temperature greater than 110°C to the deep geothermal field.

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