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Chemical And Isotopic Characterization Of The Thermal Fluids Emerging From Nestos River Delta Basin in North Greece

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Abstract. In this work we study the isotopic and hydrochemical properties of waters emerging from Nestos river delta basin (Erasmio, Eratio and Myrodato), which is forming the continental margin of the broader graben type basin of Prinos that includes the Nestos delta and the offshore extension between Thassos island and the main land around Kavala bay. Our goal is the identification of the procedures that are related to the waters' composition as well as their origin. Some of our samples are characterized by low Cl^- which excludes the marine contribution while the others present high Cl^- and Br^- which indicate marine participation. This assumption is, also, confirmed by the $\delta^{18}O$ and $\delta^{34}S$ isotopic values. Finally, we use isotopic geothermometers for the evaluation of reservoir temperature and we conclude to the existence of deep geothermal field of low to middle enthalpy, except from one sample which has middle to high enthalpy.

Keywords geothermal system, water geochemistry, O-H-S isotopes, geothermometry

1. Introduction

Isotope hydrochemistry combined with chemical analysis is a powerful tool that provides information for the origin, the recharge areas, the reservoirs's temperature and the water-rock interaction as well as the mixing processes (seawater, meteoric or magmatic fluids) (Dotsika, 2012, Dotsika, 2015). In 1970's, Institute of Geology and Mineral Exploration (I.G.M.E.) begun the geothermal investigations in Northern Greece. One of the geothermal basin in the area is Nestos Delta whose maximum depth of the 22 exploration boreholes reaches 500 m. Furthermore, the values of the geothermal gradient are very high (up to 25°C /100 m) and the water temperatures range between 40 and 72°C.

1.1 Nestos Delta basin

Nestos Delta basin is one of the hydrothermal basins whose onshore part extends over an about 450km^2 area and is part of a broader basin of Prinos which includes the Nestos delta and the offshore area between Thassos and Kavala bay. It is bounded by two major crevasses striking N70◦ and N160◦, separated from the Xanthi-Komotini basin by the basement Avdira ridge (horst). Its basement is composed by metamoprphic rocks (amphibolites, gneiss and marbles) of the Rhodope Massif and has high thermal gradient because of the granitic intrusions (Kolios, et al., 2005). In Miocene (Low-Mid), sedimentation begun with the deposition (0.7-3.0 km) sediments that are consisted of conglomerates with lignite intercalations, clastic/deltaic continental deposits and anhydrites alternating with thin layers of marls, clays and sandstones (Proedrou, 1979). Deeper in the basin, upon the clastic deposits, there is a sequence of Upper-Miocene evaporitic marine sediments, which is overlain unconformably by Plio-Quaternary sediments, that consist of clays, marine and lacustrine sediments and deltaic sandstones, (Karytsas, 1990). The geothermal fields of Erasmio (ERA) and Eratino (ERC) are the two significant low temperature fields in Nestos Delta basin.

1. Sampling and Methodology

Water samples were collected at Erasmio and Eratino fields. For the chemical analysis 12 water samples were collected in polyethylene containers of 700ml and for the isotope analysis (^{18}O, ^{2}H, ^{34}S) the samples were taken separately in two-glass bottles (50ml and 1L) at every sampling point. Additionally, temperature, pH, conductivity and alkalinity were measured directly in the field. For the determination of anions, the samples were collected untreated, while for analysis of cation the samples were filtered (0.45 μm) and acidified with HNO_3 in 1:1 proportion. For the measurement of the boron content, the fluid samples were acidified and evaporated to dryness (at 55 °C) with the presence of curcumin. The red precipitate, which is produced was dissolved in ethyl alcohol and the mixture was photometrically measured at 540nm (Eaton, et al., 1995). The chemical analysis was performed at the Institute of Geosciences and Earth Resource, C.N.R.-Pisa. The lithium was evaluated by inductively coupled plasma optical emission spectrometry with a precision of better than ±2%. The isotopic composition of oxygen ($\delta^{18}O$), hydrogen ($\delta^{2}H$) and sulfate ($\delta^{13}S$) was measured at the Stable Isotope laboratory National Center for Scientific Research "Demokritos" and the ratios were determined in water samples using the CO_2–H_2–water equilibration method (Duhr and Hilkert, 2004, Hilkert and Avak, 2004).

The isotope composition of $\delta^{2}H$, $\delta^{18}O$, $\delta^{34}S$ was measured versus Vienna Standard Mean Ocean Water (VSMOW) for hydrogen and oxygen and Canyon Diablo (CT) for sulfate. The notation δ is expressed as:

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

where R_{sample} and $R_{standard}$ are $^{2}H/^{1}H$ or $^{18}O/^{16}O$ or $^{34}S/^{32}S$ ratios of samples and standard respectively. The isotopic values were determined by the means of two or more consistent measurements of each sample, while the measurement precision was ± 1‰ for $\delta^{2}H$ and $\delta^{34}S$ and ± 0.1‰ for $\delta^{18}O$.

2. Results

The samples' temperatures, as they were measured directly in the field, range between 21 and 68 °C. The boron content ranges from 0.4 to 6.6 mg/L except one sample (ERC-5) that is 10.1 mg/L and the lithium from 0 to 1.2 mg/L, while chloride content ranges between 99.0 and 8510.4 mg/L. Here, we have to note that the maximum Cl^{-} content belongs to ERC-5. For the low-Cl^{-} samples with values lower than 200 mg/L we have to exclude the marine contribution contrary to high- Cl^{-} samples, with content greater than 200 mg/L, whose marine participation (either by mixing with seawater or by water rock interaction) cannot, obviously, be excluded. As Cl^{-} and Br^{-} ions are conservative even in geothermal systems (Dotsika, 2012, Dotsika, 2015, Dotsika and Michelot, 1992, Dotsika, et al., 2009, Henley and Ellis, 1983, Michelot, et al., 1993), they are used for the identification of chloride's and water's origin. Based on the mass equation of Cl^{-}, Br^{-} ^{18}O and ^{2}H concentrations, we calculated the seawater contributions (%) in our samples. The results are shown in Table 1. In the same table are also presented the results of the contributions calculated from oxygen and hydrogen isotopes.

Table 1. Seawater contributions (%) of the samples. MSW: mixing with seawater

Sample	Cl^{-} (mg/l)	MSW (%) Cl^{-}	Br^{-} (mg/l)	MSW (%) Br^{--}	MSW (%) ($\delta^{18}O$)	MSW (%) ($\delta^{2}H$)
ERC-1	337.0	16	20	28	24	25
ERC-2	375.8	18				25
ERC-3	5033.7	24				17
ERC-4	5264.1	25	19	27	21	14
ERC-5	8510.4	40			28	25
ERC-6	6879.2	32				
ERC-7	230.0	27	19	27	22	22
ERC-8	5800.0	12				
ERA-7	245.0	16				
ERA-8	3440.0	26			23	19
ERA-9	5570.0	26				
ERA10	5580.0	16	20	28	24	25

The $\delta^{18}O$ and $\delta^{2}H$ isotope values range from -8.6 to -5.8 ‰ and -55.5 to -42.5 ‰ 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.

We observe that the samples ERA-1, ERA-2, ERC-2 fall onto the Local Meteoric Line indicating that these samples originate from meteoric water without marine contribution. Furthermore, the samples ERC-4, ERC-5, ERC-7 and ERA-9 are shifted to the right of Local Meteoric Water Line with ERC-5 and ERC-7 falling to the seawater mixing line that represents an ideal mixing between seawater and local fresh water, which is originated by the addition and dilution of local groundwater to a deep, hot geothermal liquid of marine origin. Additionally, in Figure 2 we present the $\delta^{34}S$ and $\delta^{18}O$ isotope values of the samples in comparison with marine sulfate ($\delta^{34}S$ = 20.1‰ CD and $\delta^{18}O$ = 9.3‰

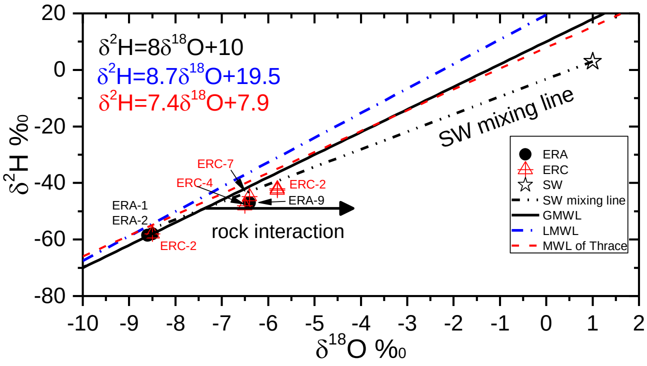

Figure 1. The $\delta^{18}O$ versus $\delta^{2}H$ isotopic values of the waters for Nestos Delta Basin. The black solid line is the Global Meteoric Water Line the blue dash-dot line is the Local Meteoric Water Line and the red dash line is the Meteoric Water Line of Thrace.

SMOW), which is very constant over the world ($\delta^{34}S$ = 20‰ CD and $\delta^{18}O$ = 9.5‰ SMOW) (Longinelli, 1989).

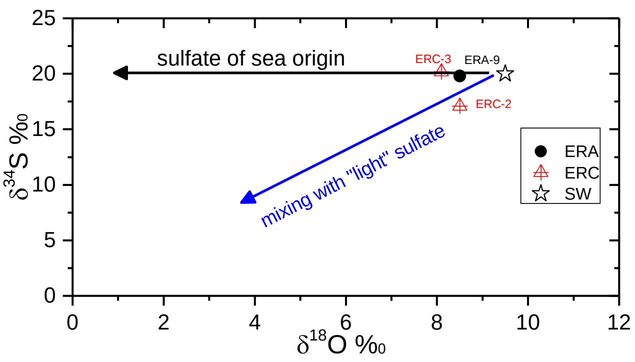

Figure 2. $\delta^{18}O$ versus $\delta^{34}S$, values of the thermal waters for all studied areas.

The sample (ERC-2) has $\delta^{34}S$ and $\delta^{18}O$ reduced compared to seawater, which indicates that there is mixing between seawater sulfates and light sulfates. The ERC-3 and ERA-9 samples have $\delta^{34}S$ values equal to seawater, whereas the $\delta^{18}O$ is lower than seawater's, which is due to the equilibrium between ^{18}O of sulfates and ^{18}O H_2O.

2.2 Geothermometry

The fluids' temperature was estimated by the following geothermometers: SiO2 (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 measured by various geothermometers are different between each other, as shown in Table 2, which is caused mainly from the marine contribution to the deep thermalfluids.

Table 2. Temperature of Erasmio (ERA) and Eratino (ERC) as calculated by the geothermometes.

Basin	**SiO_2**	**Na/K**	**Na/K/ Ca**	**Na/ Li**	**Mg/ Li**	**^{18}O SO_4-H_2O**
ERC	60-120	60-170	90-195	45-110	75-120	125
ERA	70-90	60-135	120-180	20	75	125-200

We observe that SiO_2 geothermometer temperature which is not affected by the marine participation does not agree with the maximum temperature evaluated by the Na–K and Na–K–Ca geothermometers. Moreover, the Na–Li (20-110°C) and Li–Mg (75-120°C) geothermometers also exhibit values much lower than those taken by the Na–K–Ca and Na-K but similar to those of the SiO_2. The temperatures obtained using SiO_2 geothermometer are considered to be the lowest ones, attributable to the deep hydrothermal waters. Moreover, the sulfate–water isotopic geothermometer (Lloyd, 1968, Mizutani, 1969), that is based on the equilibrium exchange of oxygen isotopes between aqueous SO_4^{2-} and H_2O, was used for the comparison with the chemical geothermometers and the temperatures calculated with it were 125 °C for ERC and 125-200 °C from ERA. Therefore, isotopic geothermometer suggests an existence of a deep geothermal field of low to middle enthalpy (120-130 °C) (ERA samples) and of middle to high enthalpy (150-200 °C) for ERC-4.

3. Conclusions

In this work we performed chemical and isotopic analysis of geothermal water from Nestos Delta basin. Our samples performed variance in chloride content with some of them having values lower than 200 mg/L while others not. The $\delta^{18}O$ and $\delta^{2}H$ values for 3 of the samples suggest mainly meteoric origin without seawater contribution while the rest of them had mixing with seawater. Finally, chemical and isotopic geothermometers were used for the evaluation of reservoir temperature, with the isotopic one suggesting an existence of a deep geothermal field of low to middle enthalpy (120-130 °C) and of middle to high enthalpy (150-200 °C).

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