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Origin of thermal waters of Nisyros volcano: an isotopic and geothermometric survey

D. Zouzias, K.St. Seymour

Department of Geology, University of Patras, Rio-Patras, GR 26 504, Greece.

dizouzias@upatras.gr; kstseymr@upatras.gr

Abstract Nisyros is characterised by a high enthalpy geothermal system. Numerous thermal springs are concentrated near the coastline with temperatures of 27°-43°C. Isotopic composition of Nisyros thermal water samples reveals mixing between *seawater* with *magmatic water* and *geothermal steam* and the possible involvement of *groundwater* and/or *meteoric water*. Combined silica and K²/Mg geothermometry indicates temperatures of 90°-140°C while deep geothermal fluids display temperatures of 245°C and steam heated samples approximately 210°C. We have calculated the initial temperature of the hot component of mixing using the diagram of dissolved SiO₂ versus enthalpy. We propose that the geothermal system of Nisyros consists of two major reservoirs. A deeper one (1400-1800 m) with temperatures greater than 245°C which is the result of mixing between *seawater* and *primary geothermal fluid* and hosts hot waters of high enthalpy which cool adiabatically and ascend, due to separation of vapours, to the shallow reservoir (0-500m) of lower enthalpy. In this mixing occurs mixing between *seawater* and *geothermal vapours* and/or *underground water* or *meteoric water* with a *hot water component* of approximately 180°-220°C. The latter is derived from the ascent of the high enthalpy waters into the shallow reservoir which represents the mixing zone of the geothermal system and is characterised by lower enthalpy compared to the deeper reservoir displaying temperatures of 90°-140°C whilst the temperature of the separated vapours are approximately 225°C.

1 Introduction

Nisyros is a complex volcano in the easternmost part of the Aegean volcanic arc with an active geothermal system of high enthalpy and reservoir temperatures above 300°C (Geotermica Italiana 1984). Two deep exploratory boreholes (NIS-1 at 1800m and NIS-2 at 1550m) have been sunk on the caldera floor by Public Power Corporation (P.P.C.) to evaluate the geothermal potential of Nisyros.

We present isotopic and geothermometric data of the thermal waters of Nisyros in order to investigate their origin and to obtain information about the temperatures of the geothermal aquifers and of the physicochemical processes that take place in the geothermal system of Nisyros. Finally, we developed a hydrological model of the thermal-fluid subsurface flow at Nisyros volcano.

2 Geological setting

Nisyros is a calcalkaline stratovolcano, the result of the subduction of the African plate under Aegean microplate. Historic phreatic activity has been reported on Nisyros from 1422 to 1888 A.D. (Vougioukalakis 1993). Seismic studies suggest a magma chamber at a depth 2 km (Papadopoulos et al. 1998). The volcanic evolution of Nisyros can be divided in two cycles: one stratovolcano-building and a second which was explosive and resulted in the formation of a caldera. Major fault systems trending NE-SW and NW-SE are related to surface geothermal manifestations such as fumarolic activity and thermal springs (Vougioukalakis 1993).

3. Sampling and analytical methods

Water samples were collected from thermal springs, boreholes and from the sea for chemical analysis during 2006-2008. Samples were subsequently filtered, acidified with ultrapure nitric acid and stored in polyethylene vials. Temperature, pH and alkalinity were measured in the field. Chemical analyses were performed using ICP/MS and ICP/EOS for major elements. Ion chromatography has been used for the determination of ions. Eight samples were collected for stable isotope analyses of $\delta^{18}\text{O}$ and δD (Table 1). Stable isotope analyses of $\delta^{18}\text{O}$ and δD were performed with precision and sensitivity of 1‰ (natural abundance) and 3‰ (enriched) for $^{\text{TMD}}$ and 0.15‰ (natural abundance) 0.4‰ (enriched) for $\delta^{18}\text{O}$, performing repeated analyses to minimize ambiguity. No admixture of Mercuric Chloride was used when collecting samples for stable isotope analyses. Additional, isotopic data from the literature were used such as the geothermal fluids of the NIS-2 geothermal borehole (Dotsika et al 2009), the sea and the thermal springs Thermiani, Pali and Loutra (Kavouridis et al. 1999; Brombach et al. 2003 and Dotsika et al. 2009), the Primary Geothermal Liquid (PGL) (Brombach et al. 2003) and the “andesitic water” of (Giggenbach 1992).

Table 1. Representative chemical and isotopic analyses of the waters of Nisyros volcano. Concentrations are in mg/l and δ values are in per mil V-SMOW. Samples NIS-1 and NIS-2 are from Dotsika et al 2009. Star indicates borehole sampling points.

Analyte Symbol	T°C	pH	Na	Mg	K	Ca	SiO ₂	NO ₃	HCO ₃	SO ₄	Cl	δ D	$\delta^{18}\text{O}$
EL-5*	35.9	6.5	129	4.45	15.3	12.3	17.3	0.03	24.4	17.6	237	-19.9	-4.92
KAS-1*	35.7	8.79	833	132	77.2	599	88.3	0.49	61	553	2220	-16.3	-4.20
MAN-41*	33.7	5.74	11800	1090	610	1050	105.8	3.3	280.6	2330	21000	6.9	0.64
PALI	27.3	6.94	5970	635	371	1220	74.4	3.3	244	1340	14000	0.6	-0.05
THERMIANI	27.4	7.57	9070	722	503	1410	104	3.3	183	1620	18400	7.3	1.52
LOUTRA	43.5	6.78	10400	637	759	1660	133.8	3.3	25.6	1600	21800	2.7	-0.02
STEF	86.7	2.28	269	34.1	55.1	62	470	2.2	335.5	155	302	17.2	10.73
Sea	22.5	7.88	13100	1400	465	470	-	3.3	176.9	2840	21500	10.9	1.41
NIS-2	290	-	21610	78	2870	7340	693	-	20	25	50390	-2.1	4.1
NIS-1	100	6.8	25290	1950	4300	17640	13	-	134	149	81500	-	-

4 Stable isotope composition of water

By plotting stable isotope composition $\delta^{18}\text{O}$ and δD of water samples from Nisyros we derive information about their origin (Fig. 1a, Table 1). The correlation function relating δD with $\delta^{18}\text{O}$ for Nisyros samples with a correlation factor $r=0.98$ is: $\delta\text{D} = 4.9\delta^{18}\text{O} + 2.8$.

Water samples EL-5 and KAS-1 (plot between the Global and Mediterranean Meteoric Lines, indicating a *meteoric origin* for these samples (Fig. 1a). The isotopic compositions of water samples from Loutra, Pali, Thermiani and MAN-41 plot along a curved mixing line (Fig. 1a) defined by the samples of meteoric origin (EL-5 and KAS-1), the Standard Mean Ocean Water (SMOW) and the Primary Geothermal Liquid (PGL) which represent the three end-members of this curved mixing line. Consequently, samples that plot between SMOW and PGL reveal mixing between these two end-members and enrichment in magmatic components while samples that plot between SMOW and the Global Meteoric Line are characterized by the contribution of seawater. Therefore, samples from Pali which plot between SMOW and the Global Meteoric line reveal a *marine origin* or waters that resulted from *mixing with seawater*. Samples from Loutra, Thermiani, MAN-41 and NIS-2 plot between SMOW and PGL and are classified as *magmatic* and/or *marine origin* waters according to the percentage of enrichment in the magmatic component (PGL) (Fig. 1a). Geothermal fluids of the NIS-2 borehole are relatively enriched in the *magmatic component* relatively to the geothermal vapors, since they plot closer to PGL revealing *magmatic origin* whilst geothermal vapors display a *magmatic-marine origin* (Fig. 1a). The thermal waters of Nisyros are the result of mixing between meteoric water, seawater and deep hot steam

suggesting seawater as the major component involved, which is consistent with their Na-Cl dominated chemistry (Table 1). Therefore, the geothermal vapors of the NIS-2 geothermal borehole participate in the mixing process of Nisyros waters coupled with transfer of heat, chemical and isotopic components. Taking this into account, Loutra samples that plot close to SMOW are of *marine origin* while samples MAN-41 that plot between SMOW and the geothermal vapors of NIS-2 represent mixtures of seawater and geothermal vapors. They display positive shifts of $\delta^{18}\text{O}$ in relation to SMOW due to enrichment in the magmatic component revealing a *marine-magmatic origin* (Fig. 1a). Thermal water samples from Thermiani spring display greater positive shifts of $\delta^{18}\text{O}$ in relation to SMOW than MAN-41 and enrichment in the magmatic component. They plot between SMOW and the geothermal vapors of NIS-2 borehole revealing a *magmatic-marine origin* (Fig. 1a). Water samples from the boiling mud-pots of the hydrothermal crater Stefanos (STEF) are the result of mixing of soil moisture with droplets of oxidized fumarolic steam precipitate. They are strongly enriched in the magmatic component and carry the isotopic identity of *Mediterranean Magmatic Waters* of Giggenbach (1997) revealing a *magmatic origin* (Fig. 1a).

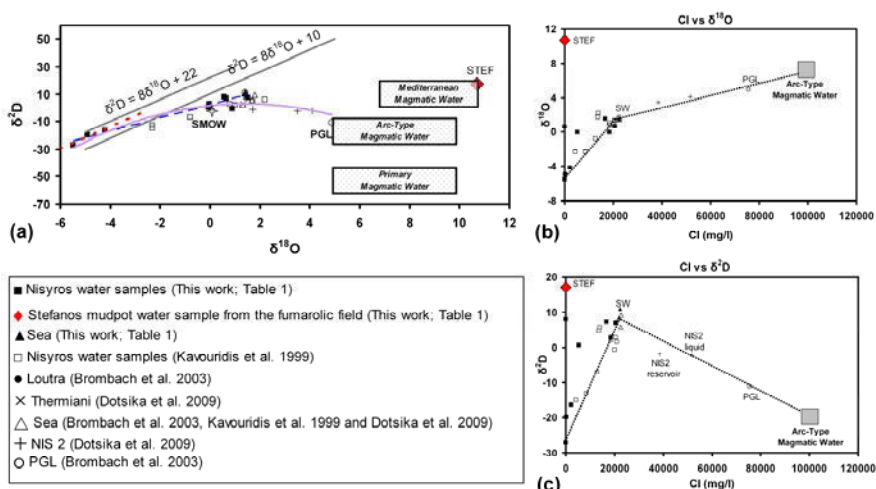


Fig. 1. (a) $\delta^{18}\text{O}$ versus $\delta^2\text{D}$ isotopic composition for Nisyros water samples. Red line indicates the correlation function of meteoric origin waters. Blue line indicates the correlation function of all Nisyros water samples. Mixing processes between three components (meteoric water, sea-water, primary geothermal liquid) are indicated by a purple curved line. (b, c) $\delta^{18}\text{O}$ and $\delta^2\text{D}$ isotopic composition versus Cl concentrations for all Nisyros water samples.

The origin of the Primary Geothermal Fluid (PGL) is attributed to mixing between the Arc-Type Magmatic Water of Giggenbach (1992) and the local sea-water (Brombach et al. 2003; Marini and Fiebig 2005; Dotsika et al. 2009). In view of the participation of magmatic water in the Nisyros geothermal system, a plot of Cl versus $\delta^{18}\text{O}$ and $\delta^2\text{D}$ (Fig. 1b and 1c) indicates that the geothermal fluid

of NIS-2 can be considered as a mixture of approximately 40% of the primary geothermal liquid (PGL) and 60% of the local seawater, in agreement with Dot-sika et al. (2009). Taking into account the isotopic composition of fumaroles from Stefanos and Polyvotis hydrothermal craters (Kavouridis et al. 1999) which plot close to PGL, we conclude that mixing in the Nisyros geothermal system involves local seawater, magmatic water, geothermal steam and the possible involvement of local groundwater and/or meteoric water.

5 Geothermometry

Surface temperatures of the thermal waters samples from Nisyros range from 27° to 43°C (Table 1). Since these water samples are characterized by mixing and water-rock interactions, we consider the cation geothermometry as unreliable.

Quartz and quartz steam loss geothermometers (Fournier, 1977) of these waters indicate a temperature range from 115° to 140°C for the Nisyros samples (Table 2). However, since the quartz geothermometer probably works best in the temperature range 150-225°C, for temperatures below 150°C the solubility of silica is controlled by chalcedony or cristoballite (Fournier 1977).

Table 2. Calculated subsurface reservoir temperatures from the thermal waters using quartz, quartz steam loss geothermometers (Fournier 1977) and dissolved silica versus enthalpy calculations for the initial temperature of hot component of mixed waters (Truesdell and Fournier 1977).

	Quartz	Quartz steam loss	SiO ₂ vs. enthalpy		Quartz	Quartz steam loss	SiO ₂ vs. enthalpy
EL-5	49	56	112.95	Loutra	139	134	218.82
KAS-1	117	115	180.66	Thermiani	125	122	220.98
Pali	108	108	206.12	STEF	224	204	227.32
MAN-41	126	123	191.28	NIS2	258	230	233.7

Chemical systems based on dissolved SiO₂ and the water component of K and Mg provide evidence of the water-rock interaction temperatures just before water discharge (Fig. 2). Nisyros samples plot along the conductive cooling line after fully equilibrating with chalcedony at temperatures of 90°-140°C (Fig. 2). This agrees with the temperatures calculated by silica geothermometry, where the solubility of silica is controlled by chalcedony (Table 2). Sample EL-5 differs from the others probably due to dilution with meteoric water (Fig. 2). Sample NIS-2 plots along the equilibrium line of quartz corresponding to adiabatic cooling and displays temperatures of 245°C (Fig. 2) relatively close to the temperatures of 290°C (>350°C) measured in geothermal drilling. Sample STEF displays high silica content and temperatures of approximately 210°C (Fig. 2) in agreement with the temperatures calculated by silica geothermometry (Table 2).

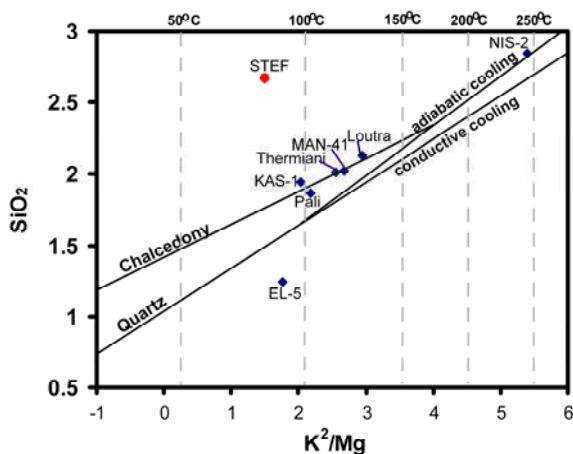


Fig. 2. Log of silica concentrations (Log SiO₂) versus (Log K²/Mg) of Nisyros thermal waters comparing silica (Fournier 1977) and K-Mg-based (Giggenbach et al. 1983) geothermometers.

We testify also here the existence of two major reservoirs which are located at depths of 0-500 m for the shallow one and 1400-1800 m for the deeper one (Geotermica Italiana 1984). These two reservoirs are characterized by temperatures of 90°-140°C and over 245°C respectively. The geothermal reservoirs of Nisyros are at higher than boiling surface temperatures; therefore, the hot fluid is cooled adiabatically and ascends to the surface separated from steam (Fournier 1977). Since mixing in the Nisyros geothermal system takes place between hot and cold waters it is necessary mixing to be taken into consideration in the calculations of reservoir temperatures. Truesdell and Fournier (1977) proposed a simplified procedure of calculating the initial temperature of the hot component of mixing using the diagram of dissolved SiO₂ versus enthalpy. We have calculated the reservoir temperatures of the mixing zone applying the methodology as described by Fournier (1977) for waters subjected to mixing where enthalpy of the hot water in the mixing zone is less than the enthalpy of the hot water in the depth due to separation of steam during ascent (Table 2). Samples KAS-1, MAN-41, Loutra, Pali and Thermiani display temperatures of 180° to 220°C, which are much lower than the temperatures of 290°C measured in the NIS-2 at depth 1550m (Geotermica Italiana 1984). This occurs since the enthalpy of hot water in the shallow reservoir (0-500m) in the mixing zone is less than the enthalpy of hot water in the deeper reservoir (1400-1800m) due to separation of steam during ascend of the thermal fluid. Sample STEF is heated by the fumarolic activity and display temperature of approximately 225°C which corresponds to the temperature of the separated vapours from the adiabatically cooled hot water that ascends to the mixing zone. Sample EL-5 has lower temperatures (~113°C) and probably is governed by leaching and dissolution of minerals.

6 Discussion and Conclusions

Surface temperature of the thermal water samples from Nisyros range from 27° to 43°C and are the result of mixing between seawater, meteoric water and deep hot steam. Seawater is the major component involved, consistent with their chemistry which is dominated by Na and Cl (Table 1). Isotopic compositions of Nisyros thermal waters plot along a curved mixing line (Fig. 1a) where samples that plot between SMOW and Primary Geothermal Liquid (PGL) reveal mixing between these two end-members and enrichment in a magmatic component. Samples between SMOW and the Global Meteoric Line are characterized by seawater contribution. Samples from Pali reveal a *marine origin* and samples from Loutra, Thermiani, MAN-41 and NIS-2 a *magmatic* and/or *marine origin* according to the percentage of enrichment in the magmatic component (Fig. 1a). The geothermal fluid of NIS-2 borehole can be considered as a mixture of approximately 40% of PGL and 60% of local seawater (Fig. 1b and 1c) in agreement with Dotsika et al. (2009). Taking into account the isotopic composition of fumaroles from Stefanos and Polyvotis hydrothermal craters from Kavouridis et al. (1999) which plot close to PGL we conclude that mixing in the Nisyros geothermal system takes place between *local seawater* with *magmatic water* and *geothermal steam* and the possible involvement of *local groundwater* and/or *meteoric water*.

Quartz and quartz steam loss geothermometers (Fournier 1977) indicate a temperature range from 115° to 140°C for the Nisyros samples (Table 2). However, since the temperatures are below 150°C the results should be treated carefully. In the chemical system based on dissolved SiO₂ and the water component in K and Mg, Nisyros samples display temperatures ranging from 90° to 140°C (Fig. 2) which agree with temperatures calculated by silica geothermometry (Table 2). Sample NIS-2 displays a temperature of 245°C relatively close to the temperature of 290°C measured in the geothermal drilling (Geotermica Italiana 1984). Sample STEF displays a temperature of approximately 210°C (Fig. 2) in agreement with the temperatures calculated by silica geothermometry (Table 2).

Since mixing in the Nisyros geothermal system takes place between hot and cold waters we have calculated the initial temperature of the hot component of mixing using the diagram of dissolved SiO₂ versus enthalpy. The initial temperature of the hot component calculated for the Nisyros waters display temperatures of 180° to 220°C, much lower than the temperature of 290°C (>350°C) measured in the NIS-2 geothermal borehole at depth 1550 m (Geotermica Italiana 1984). This occurs since the enthalpy of hot water in the shallow reservoir (0-500; Kavouridis et al. 1999) in the mixing zone is less than the enthalpy of hot water in the deeper reservoir (1400-1800 m; Geotermica Italiana 1984) due to separation of steam during geothermal fluid ascent. Temperatures of approximately 225°C for sample STEF correspond to the temperature of the separated vapours of the adiabatically cooled hot water that ascends to the mixing zone. Sample EL-5 has lower temperatures (approximately 113°C) and probably is governed by leaching and dissolution of minerals.

We propose that the geothermal system of Nisyros consists of two major reservoirs. The deeper one (1400-1800 m) with temperatures greater of 245°C (Fig. 2) is the result of mixing between *local seawater* and *primary geothermal fluid* (PGL) (Fig. 2) and hosts hot waters of high enthalpy which cool adiabatically and ascend due to separation of vapours to the shallow reservoir of lower enthalpy. The shallow reservoir (0-500 m) is the result of mixing between *local seawater* and *geothermal vapours* and/or *underground water* or *meteoric water* (Fig. 1a) with a *hot water component* of approximately 180° to 220°C temperatures derived from the ascent of the high enthalpy waters due to separation of vapours and represents the mixing zone of the geothermal system which is characterised by lower enthalpy in relation to the deeper reservoir with temperatures ranging ranges from 90° to 140°C while the temperature of the separated vapours are approximately 225°C.

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