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MUDPOTS AT STEFANOS HYDROTHERMAL CRATER OF NISYROS VOLCANO. AN INSIGHT AT THE HYDROTHERMAL PROCESSES OF AN ACTIVE VOLCANO

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Abstract

On Nisyros island as a result of the volcanic activity and active tectonic, a hydrothermal system develops and it is expressed by 5 types of surface manifestations: i) thermal springs, ii) fumaroles iii) hydrothermal craters, iv) hot grounds and v) mudpots. In general, a mudpot could be described as an acidic [hot spring](https://en.wikipedia.org/wiki/Hot_spring) and [fumarole](https://en.wikipedia.org/wiki/Fumarole) with limited water which it is formed in high-temperature geothermal areas. Water sample and depositions of mudpots collected, analyzed and studied from Stefanos hydrothermal crater, which is the only site on Nisyros Island, where mudpots occur. Mudpots water is very acidic (pH=2.4), with high sulfate concentration (1375mg/L), due to the H2S(gas) and temperature near the boiling point. As a result, elemental sulfur is found inside the depositions alongside with products of the hydrothermal alteration of the surrounding rocks. In the water and in the depositions were found high concentrations in several elements (e.g. in water: 55mg/L Fe; 19.5mg/L Zn, in depositions: 430mg/Kg Pb; 72mg/Kg Cu; 60mg/Kg Cr) reflecting the alterations processes which are taking place.

Keywords: mudpots, hydrothermal systems, volcano, Nisyros, Greece.

Περίληψη

Στο νησί της Νισύρου, σαν αποτέλεσμα της ηφαιστειακής δραστηριότητας και των ενεργών τεκτονικών διεργασιών, αναπτύσσεται ένα υδροθερμικό σύστημα, το οποίο παρουσιάζει πέντε τύπων επιφανειακές εκδηλώσεις: α) θερμές πηγές, β) ατμίδες γ) υδροθερμικούς κρατήρες, δ) θερμά εδάφη και ε) αναβράζουσες ηφαιστειακές λίμνες λάσπης. Οι αναβράζουσες ηφαιστειακές λίμνες λάσπης μπορούν να περιγραφούν και σαν όξινες θερμές πηγές ή ατμίδες, με περιορισμένη ποσότητα νερού, σε υψηλής θερμοκρασίας ηφαιστειακά περιβάλλοντα. Κατά την παρούσα μελέτη, ελήφθησαν δείγματα νερού και αποθέσεων από τον υδροθερμικό κρατήρα του Στέφανου. Η περιοχή του κρατήρα είναι το μόνο σημείο στο οποίο εμφανίζονται αναβράζουσες ηφαιστειακές λίμνες λάσπης στη Νίσυρο. Το νερό είναι ιδιαιτέρα όξινο (pH=2.4), με υψηλές συγκεντρώσεις θεϊκών (1375mg/L), λόγω του αερίου H2S) και θερμοκρασία κοντά στο σημείο βρασμού. Αποτέλεσμα του γεγονότος αυτού είναι η δημιουργία του στοιχειακού θείου σε κρυστάλλους που εντοπίζεται στις αποθέσεις. μαζί με προϊόντα της υδροθερμικής εξαλλοίωσης των περιβαλλόντων πετρωμάτων. Κατά τη χημική ανάλυση του νερού και των αποθέσεων εντοπίστηκαν υψηλές συγκεντρώσεις σε μια σειρά *στοιχείων (π.χ. στο νερό: 55mg/L Fe; 19.5mg/L Zn, στις αποθέσεις: 430mg/Kg Pb; 72mg/Kg Cu; 60mg/Kg Cr) σαν αποτέλεσμα των διεργασιών της υδροθερμικής εξαλλοίωσης που λαμβάνει χώρα στην περιοχή. Λέξεις κλειδιά: αναβράζουσες λίμνες λάσπης, υδροθερμικά συστήματα, ηφαίστειο, Νίσυρος, Ελλάδα.*

1. Introduction

Nisyros Island is located in southeastern part of Aegean Sea and geologically belongs to the South Aegean active volcanic arc. The whole island forms a calc-alkaline stratovolcano, which is built at various explosive activities in the last 150,000 years; it has a 3.8 km diameter caldera (Di Paola, 1974; Keller *et al*., 1990; Vougioukalakis, 1993; Francalanci *et al*., 1995) and is currently classified in the "Very High Threat" category (Kinvig *et al*., 2010).

As a result of the volcanic activity and active tectonic, a hydrothermal system occurs. The presence of hydrothermal activity on Nisyros is expressed by five types of surface manifestations: i) the thermal springs distributed along the northern and southern coasts of the island, ii) the large fumarolic field located mainly in the southern Lakki plain, iii) the hydrothermal craters, iv) the hot grounds and v) the mudpots located in the center of Stefanos hydrothermal crater (Fig. 1, 2). In the Lakki area, different hydrothermal eruptions took place recently until the historical times (Marini *et al.,* 1993). Also, changes in the composition of the fumaroles recorded recently (1995-1998) and they were associated with episodes of intense seismicity and ground deformation (Chiodini *et al*., 2002; Caliro *et al*., 2005; Shimizu *et al*., 2005), during a volcanic unrest period.

In general, mudpot or mud pool could be described as an acidi[c hot spring](https://en.wikipedia.org/wiki/Hot_spring) or [a fumarole](https://en.wikipedia.org/wiki/Fumarole) with limited water. It usually takes the form of a pool of bubblin[g mud.](https://en.wikipedia.org/wiki/Mud) The acid fluids and microorganisms alter the surrounding rock into clay and mud. The mud of a mudpot usually takes the form of a [viscous,](https://en.wikipedia.org/wiki/Viscosity) often bubbling [slurry.](https://en.wikipedia.org/wiki/Slurry) As the boiling mud is often squirted over the brims of the mudpot, a sort of mini-crater of mud could build up (Clynne *et al.*, 2003).

Mudpots are forming high-temperature geothermal areas where water is in short supply. The little water that is available rises to the surface usually at spots where are rich in volcanic ash, clay and other fine particulates. The thickness of the mud usually changes along with meteoric phenomena, i.e. rain. On Nisyros Island mudpots were detected only at Stefanos hydrothermal crater (Fig. 2) and their size depends on climate conditions i.e. the rain in the Stefanos and surrounding plain and caldera area.

The aim of this paper is to study the chemical composition of the mudpots and the mineralogical and geochemical composition of their depositions and relate them with the hydrothermal processes of Nisyros volcano.

2. Geological setting

Nisyros island $(42 \text{ km}^2 \text{ in surface})$ is a small and young composite volcano with a central caldera (Keller, 1971; Di Paola, 1974; Vougioukalakis, 1984, 1993; Limburg, 1986; Limburg *et al*., 1986; Bohla and Keller, 1987; Lodise, 1987; Seymour and Vlassopoulos, 1992; Wyers and Barton, 1989; Keller *et al*., 1990; Papanikolaou *et al*., 1991; Limburg and Varekamp, 1991; Gansecki, 1991; Francalanci *et al*., 1995; Volentik *et al*., 2002) (Fig. 1). The topography resembles the shape of a truncated cone with a basal diameter of 8 Km and a central caldera depression of 4 Km diameter. The post-caldera domes (youngest volcanic products) excel the caldera rim $\left(\sim 450 \text{ m high}\right)$ and the internal domes arrive at a maximum height of 698 m. The whole island is entirely buildup of volcanic products, deposited on a basement consisting of Mesozoic limestone and Neogene sediments (Barberi *et al*., 1988; Varekamp, 1992; Nis-1 well report - Geotermica Italiana, 1983).

Two eruptive cycles are distinguished in the evolution of Nisyros volcanic activity: the first cycle includes the cone-building eruptive activity and the second one the caldera-forming eruptive activity. The second cycle consists of two different phases. Each phase commenced with a low intensity - low magnitude phreato-magmatic explosion fed by rhyolitic magmas. This triggered a central calderic collapse that was followed by extrusion of rhyolitic-dacitic domes and lava flows.

The existing radiometric ages (K-Ar, ¹⁴C), tephro-stratigraphy and the absence of the Kos Plateau Tuff deposits suggest that the actual subaerial part of Nisyros was built up during the last 160,000 years. The available radiometric ages of Nisyros rocks are difficult to correlate and still leave some open questions about the time frame of volcanic eruption. K/Ar ages of 66.4 and 24 ka were obtained on the uppermost products of the cone building activity (Rehren, 1988). According to these data, the earliest caldera collapse should have an age $<$ 24 ka. Nevertheless, ages $>$ 44 ka were obtained with different methods for the Nisyros Upper Pumice deposits, whereas the age of the Yali Upper Pumice that postdate the last Nisyros caldera collapse is 31 ka (Yali C deep ash layer of Federman and Carey, 1980).

All the historically registered explosions at Nisyros (1873-1887) are hydrothermal and created three small craters in the west area of the caldera floor (Gorceix, 1873, 1874; Martelli, 1917). The presence of more than 8 older hydrothermal explosion craters in the caldera floor, with a maximum diameter of 300m, indicate that this type of activity was frequent in the past few thousand years. The island is today a site of intense hydrothermal activity which feed many fumaroles in the caldera floor area and hot springs along the coast, hosting a high enthalpy geothermal field (fluids with more than 400°C at 1800m depth; Geotermica Italiana, 1983).

Active tectonics is prominent on the Nisyros island group. Some of the active faults have been reactivated during seismic crisis manifested in the last century. During the last 1995-1997 volcanic unrest shallow earthquake activity, two of these fractures trending N-S and NW-SE were opened on Nisyros and Yali, respectively (Vougioukalakis *et al*., 1998).

Nisyros is characterised by a nearly continuous series of rocks, from basaltic andesites to rhyolites. Basaltic andesites and most of andesites are CA, whereas dacites and rhyolites plot along the boundary between CA and HKCA series.

3. Materials and methods

3.1. Groundwater and depositions sampling and analysis

From mudpots, which are located at the Eastern part of Stefanos hydrothermal crater (Fig. 2), one hot groundwater sample and several wet and dry samples from the depositions were collected. The groundwater sample was vacuum filtered and stored in polyethylene bottles and preserved in a refrigerator. Part of it was acidified to a final concentration of 2% nitric acid. Sampling was conducted on June 2015.

About the groundwater sample, the major elements and ion concentrations were measured by spectrophotometry, or/and titration or/and AAS or and ICP-OES (Table 1). The trace element concentrations were measured using ICP-MS (Table 1).

Depositions from active (wet) and dry mudpots were collected. The deposition samples were dried in an oven at a temperature of 40° C and afterwards pulverized to < 200 mesh in an agate mill. Representative samples were digested with a mixture of $HCl-HNO₃-HF$ acids and were analysed for a series of trace elements by ICP-MS and a series of major elements by ICP-OES after fusion. In order to determine the mineralogical composition of the samples, a number of thin sections were prepared and investigated under optical microscope and powder X-ray diffraction (XRD) analyses were conducted. The XRD study was carried out using a Philips X'Pert Panalytical X-ray diffractometer, operating with Cu radiation at 40 kV, 30 mA, 0.020° step size and 1.0 s steptime. The XRD patterns were evaluated using the EVA ver. 11 software. All samples were analyzed in the Laboratories of Institute of Geology and Mineral Exploration (I.G.M.E.) in Athens.

Figure 1 - 3D simplified geological map of Nisyros Island (Vougioukalakis and Androulakakis, 2008).

Figure 2 - (A) General view of the Nisyros caldera from the North. (B) General view of the Stefanos hydrothermal crater, with characteristic white-yellowish altered rocks. (C) and (D) Dry mudpots. (E) Steaming ground with limited water supply. (F) Active boiling mudpot.

4. Analytical results

The analysed chemical parameters are presented in Table 1 and 2. The studied water sample is very acidic (pH = 2.4) with high concentration of sulfate (1375 mg/L), silica (277 mg/L SiO₂), calcium (190 mg/L) and aluminum (72 mg/L) . It presents also high concentrations of metallic elements like Fe (55 mg/L) and Zn (19.5 mg/L).

The mineralogical and geochemical compositions of depositions, from the active and dry mudpots, are similar. The mineralogical composition of the depositions is quartz, tridymite, alunite, elemental sulfur, chlorite-vermiculite-montorillonite, kaolinite, barite and halite (Fig. 3). The bulk geochemical analysis (Table 2) of the studies depositions shown high concentrations to major elements like 55 % to SiO₂ and 14.7 % to S and between 1 to 2 % to Al₂O₃, K₂O and Na₂O. High concentrations were found in a series of trace elements and some REE like Pb (up to 430 mg/Kg), Cu (up to 72 mg/Kg), Cr (up to 60 mg/Kg), As (up to 37 mg/Kg), Zn (up to 35 mg/Kg), Ni (up to 16 mg/Kg), Ce (up to 27 mg/Kg), La (up to 15 mg/Kg), Nd (up to 10 mg/Kg) and Th (up to 5 mg/Kg).

5. Discussion - conclusions

Nisyros Island is young composite volcano with a central caldera. Underneath, it develops a hydrothermal system, with circulation of meteoric and sea water. Surface manifestations of the hydrothermal system are the hot springs, the fumaroles, the hydrothermal craters, the hot grounds and the mudpots. The present study shows and evaluates for the first time the chemical composition of the active mudpots of Nisyros and the mineralogical and geochemical composition of their depositions.

On Nisyros, meteoric and sea water goes deep underground using permeable rock, fractures, fault systems and boundaries between volcanic flows. Once deep underground, the water is heated. The heat source is a body of magma or a body of solid but still very hot rock related to recent quite active volcanism. This heat source is probably located at a depth of 4-6 km. When water penetrates the hot rock surrounding the heat source, it is heated by conduction. Hydrochloric acid, sulfurous gases and other volatiles emitted by the body of magma or hot rock dissolve in the water as it is heated. Because it is less dense than cold water, the heated water rises by convection. As the water rises, acids react with surrounding rocks, enriching the water in dissolved silica $(SiO₂)$ and metals. The chemically evolving hot water rises, where it saturates permeable rock and accumulates in fractures beneath the thermal features creating a geothermal reservoir. Based on the two deep geothermal wells drilled on the island by PPC (Public Power Company, Geotermica Italiana, 1983, 1984; Marinelli *et al*., 1983; Chiodini *et al*., 1993) two main hot aquifers were identified. The first one in ~250-700 m and the second one from ~1000 to 1500 m depth, with temperatures 120-180 $^{\circ}$ C and 290 $^{\circ}$ C respectively (Marini *et al*., 1993; Ambrosio *et al*., 2010).

When rising hot water reaches a depth where the pressure of overlying fluid (hydrostatic pressure) has decreased, boiling occurs. Bubbles of steam rise through the water and migrate to the surface, carrying most of the gases that were dissolved in the water (carbon dioxide, hydrogen sulfide, hydrogen, nitrogen and helium).

Steam and non-condensable gasses reaches the surface through fractions and creates the fumaroles. It may also condense and heat groundwater near the surface. The condensed steam and heated water may boil at the water table, creating the boiling mudpots. Hydrogen sulfide gas is oxidized in this near-surface, oxygen-rich environment to form elemental sulfur and sulfuric acid, producing waters that are acidic (low pH) and have a high sulfate concentration. Stefanos mudpots water have $pH =$ 2.4, 1375 mg/L of sulfate and temperature near the boiling point. Also, hydrogen sulfide gas is one of the main components of the fumaroles in Nisyros volcano (Teschner *et al*., 2005; Tassi *et al*., 2013). For that reason, also the studied water present very high sulfate concentration (1375 mg/L) and crystals of elemental sulfur found inside the studied depositions. The water is also enriched in dissolved silica (277 mg/L $SiO₂$) and metals (e.g. 55 mg/L Fe; 19.5 mg/L Zn). High concentrations of major and trace elements like Ca (190 mg/L), Al (72 mg/L), Sr (480 μg/L) etc reflecting the alterations processes which are taking place.

Inside Stefanos hydrothermal crater characteristic is the view of white-yellow altered rocks (Fig. 2A, B, C). Hydrothermal alteration occurs when acidic hot water chemically changes minerals in rocks. The final product of such alteration in volcanic rocks is usually white material rich in kaolinite clay and silica; this material is abundant at Nisyros caldera and especially at Stefanos hydrothermal crater. More specifically, the mineralogical study reveals that the studied depositions comprise of quartz, tridymite, alunite, elemental sulfur, chlorite-vermiculite-montorillonite, kaolinite, barite and halite as main mineral phases. In agreement to the mineralogical results are the results of the chemical analysis. The highest concentrations are presented to $SiO₂$ and S (52 % and 14.7 %) respectively) and follow A_1O_3 , K_2O and Na_2O with concentrations between 1 to 2 %. It is interesting the enrichment of the depositions in metals like Pb (up to 430 mg/Kg), Cu (up to 72 mg/Kg), Cr (up to 60 mg/Kg), As (up to 37 mg/Kg), Zn (up to 35 mg/Kg), Ni (up to 16 mg/Kg) and in some REE like Ce (up to 27 mg/Kg), La (up to 15 mg/Kg), Nd (up to 10 mg/Kg) and Th (up to 5 mg/Kg).

Even though the presented data are limited, allow as insights of the hydrothermal processes of Nisyros volcano. In order to have a better picture, a further more systematic study of the mudpots is needed i.e. including chemical and isotopic analysis of the gas and isotopic analysis of the water. Several studies have conducted concerning Nisyros, but still many open questions remain to be answered. More data concerning the reservoir, the circulation and the composition of the fluid below the surface will be valuable. They could reveal the detail hydrothermal processes which are taking place and allow us to compare them with old-not active systems, estimate geothermal potentials of the system etc. Also, the surface manifestations of the system create an extreme environment in which unstudied geological and biological processes take place alongside.

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