

Geochemical indicators of possible ongoing volcanic unrest at Nisyros Island (Greece)

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Received 8 November 2001; revised 11 February 2002; accepted 20 February 2002; published 17 August 2002.

[1] Significant changes occurred in the chemistry of gases discharged from Nisyros fumaroles in the years, 1997–2001, following a strong seismic crisis. Increasing H_2S/CO_2 ratios and decreasing CH_4/CO_2 ratios are attributed to an increased contribution of magmatic fluids to the hydrothermal system. Some fumaroles showed concurrent increases in H_2 and CO contents implying increases in temperature and pressure in the upper parts of the hydrothermal system. These changes reinforce the possibility of an increased hazard of hydrothermal eruptions at present with respect to the '90's. Moreover, both the present events and the historical hydrothermal eruptions may represent precursory signals of a new period of volcanic unrest at Nisyros. *INDEX TERMS*: 8424 Volcanology: Hydrothermal systems (8135); 8419 Volcanology: Eruption monitoring (7280); 1099 Geochemistry: General or miscellaneous

1. Introduction

[2] Nisyros volcanic island, built up during the last 100 ka, lies at the eastern end of the Aegean active volcanic arc (Figure 1). Its volcanic activity has been characterized by (i) an early submarine stage, (ii) a subaerial cone-building stage, culminating in the formation of a central caldera, and (iii) a post-caldera stage, when several dacitic-rhyolitic domes were extruded [e.g., Keller, 1982]. The last magmatic activity of Nisyros is of unknown age and no magmatic eruption occurred during historical times.

[3] However, hydrothermal eruptions were frequent in historical times. They affected the southern part of the Lakki plain and the Lofos dome, presently the site of widespread fumarolic activity (Figure 1). The last hydrothermal eruptions took place in 1871–1873 and 1887 [Marini *et al.*, 1993 and references therein]; they formed the craters of Polybotes and Phlegethon (1871–1873) and Polybotes Micros (1887).

[4] Based on historical reports, it seems likely that seismic shocks played a fundamental role in triggering at least the last hydrothermal eruptions [Marini *et al.*, 1993]. Earthquakes were responsible for fracture opening, permitting a sudden uprise of deep hot fluids towards the surface. A strong seismic crisis again affected Nisyros island in 1996–1997 [Papadopoulos *et al.*, 1998]. This crisis did not trigger any hydrothermal eruptions, but was followed by important variations in the chemistry of fumarolic gases. The aim of this work is to investigate these chemical changes and their significance for the volcanic surveillance of Nisyros volcano. The study is based on previous chemical and isotopic data for the fumaroles [Chiodini *et al.*,

1993a; Brombach, 2000 and references therein] and new data collected in 2000 and 2001, in the framework of the European Union project GEOWARN. Sampling and chemical analyses were carried out following standard methodologies [Chiodini *et al.*, 2001 and references therein]. Analytical data are available from the authors.

2. Background Information and Chemical Changes of the Fumaroles

[5] Fumarolic activity and the location of hydrothermal craters are chiefly related to a main NW- and NE-trending active fault systems [Marini *et al.*, 1993; Papadopoulos *et al.*, 1998; Figure 1]. The westernmost NE-SW faults, acting as pathways for the fumaroles of the Lofos dome area (Polybotes Megalos PG, Polybotes Micros PP, and Phlegethon PH), and the easternmost NE-SW faults, feeding the Kaminakia fumaroles (K), are both visible in the field. The buried NE-SW fault controlling the Stephanos fumaroles (S) has instead been recently revealed by a detailed diffuse CO_2 -flux survey [GEOWARN, OV, unpublished data].

[6] All the fumaroles have outlet temperatures close to the boiling point of water (96–100°C). Their main components are H_2O followed by CO_2 and H_2S , while N_2 , H_2 , CH_4 , CO, Ar, and He are minor components. The absence of strongly acid gases (i.e. SO_2 , HCl, HF) and the relatively high CH_4/CO ratios indicate that fumarolic effluents are generated from a boiling hydrothermal liquid rather than from direct magma degassing [Chiodini *et al.*, 1993a]. However, the involvement of a magmatic component in the recharge of the hydrothermal aquifers of Nisyros is suggested by the δD and $\delta^{18}O$ values of fumarolic condensates, as well as by the $\delta^{13}C$ values and the He/ N_2 and He/Ar ratios of fumarolic gases [Brombach, 2000]. It is also evidenced by their relatively high $^3He/^4He$ ratios (R/Ra from 3.1 to 5.4) [Dietrich *et al.*, 1999].

[7] Previous studies of Nisyros fumaroles were mainly aimed at understanding and refining the geochemical model of the local hydrothermal-magmatic system, largely based on subsurface data acquired from two deep geothermal wells, Nis-1 and Nis-2, drilled and sampled in the '80s [Chiodini *et al.*, 1993a; Figure 1]. Unfortunately, these wells were sealed after a few years and are not accessible at present. According to the geochemical model by Chiodini *et al.* [1993a], the hydrothermal system of Nisyros is made up of a $\sim 300^\circ C$ deep reservoir, sited at depths >1000 m, and of shallower systems, with temperature of 150–250°C.

[8] The large changes in the chemistry of Nisyros fumaroles, which occurred in 1997–2001, comprise (Figure 2): (a) a dramatic increase in the H_2S/CO_2 ratio and a decrease in the CH_4/CO_2 ratio

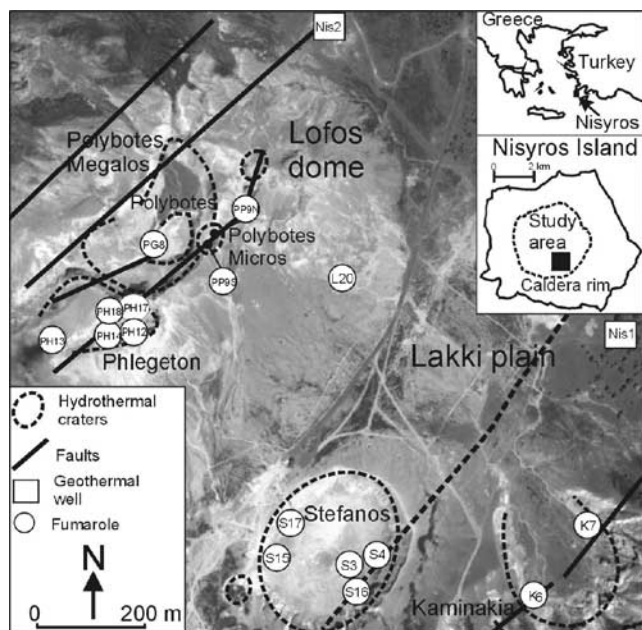


Figure 1. Sample location map in the hydrothermal field with hydrothermal eruption craters within the Nisyros caldera. The picture is part of the orthorectified IKONOS satellite image.

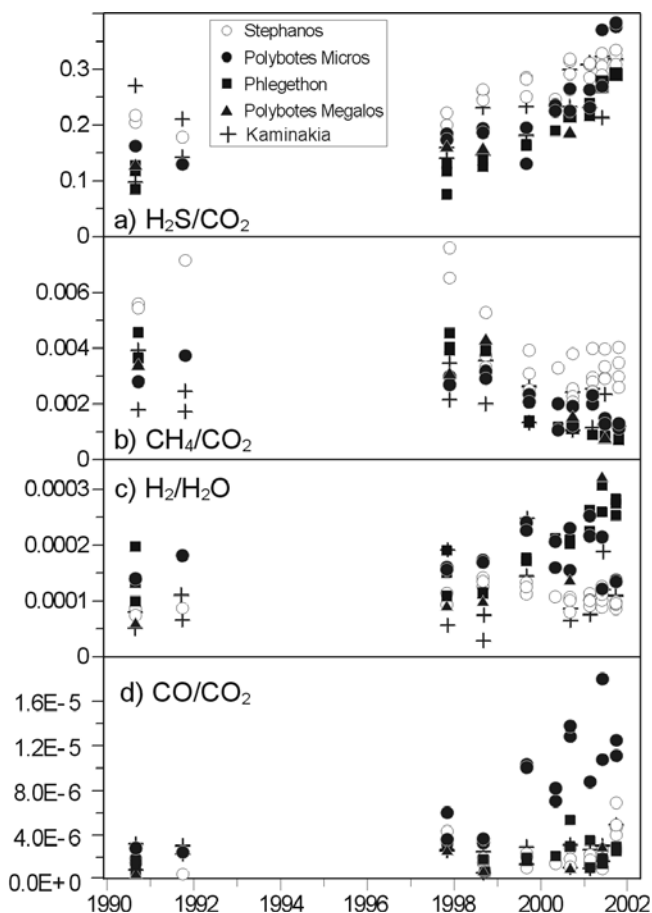


Figure 2. Time variation diagrams for (a) H_2S/CO_2 ratios, (b) CH_4/CO_2 ratios, (c) H_2/H_2O ratios, and (d) CO/CO_2 ratios. In order to plot the Kaminakia samples in the same diagrams the H_2S/CO_2 ratio was multiplied by 3, the CH_4/CO_2 ratio divided by 10, and the H_2/H_2O ratio by 3.

for all fumaroles, and (b) an increase in H_2/CO_2 and in CO/CO_2 for some fumaroles only.

3. Discussion

[9] The increase in the H_2S/CO_2 ratio and the concurrent decrease in the CH_4/CO_2 ratio, observed for all the Nisyros fumaroles is investigated in the H_2S/CO_2 vs. CH_4/CO_2 diagram of Figure 3. Apart from the peripheral Kaminakia fumaroles, characterized by relatively high CH_4 and low H_2S contents, Figure 3 shows two well-defined, convergent trends: one for S fumaroles and the other one for Lofos vents. The samples collected during 2001 plot at the intersection of these two trends, indicating a general homogenization of the chemical composition of these fumaroles.

[10] Different interpretations are possible to explain these concurrent changes. Because of the different solubilities of H_2S , CO_2 , and CH_4 , the observed variations could be ascribed to an increase in the fraction of steam separated at depth through boiling of the hydrothermal aquifer. In turn, this increase in steam fraction could result from either increasing temperature of the hydrothermal aquifer (input of heat without matter) or depressurization of the system (opening of additional conduits above the aquifer). This interpretation is formally equivalent to the concept of early and late vapor separation through progressive boiling of a closed aquifer: early vapors are enriched in sparingly soluble gases, whereas late vapors are richer in highly soluble volatiles [Giggenbach, 1997]. This interpretation, however, is not fully supported by analytical data, because decreasing trends similar to that for CH_4 should characterize other sparingly soluble gases, such as the inert species N_2 and He, which instead remained relatively constant during the study period.

[11] Relative increases in most soluble gases have also been observed for fumaroles directly fed by a degassing magma batch, such as at Showa-Shinzan, Usu volcano, Japan [Symonds et al., 1996]. In this case, decreasing C/S and S/Cl ratios between 1954 and 1985 were interpreted as due to progressive outgassing of the less soluble components ($Cl > S > C$) from a closed magma reservoir. A similar simple interpretation cannot be proposed for Nisyros, since a hydrothermal system is interposed between the degassing magma and the surface. However, it is possible that from 1997 to 2001 the Nisyros hydrothermal system was affected by a progressively increasing input of magmatic gases. The increase in

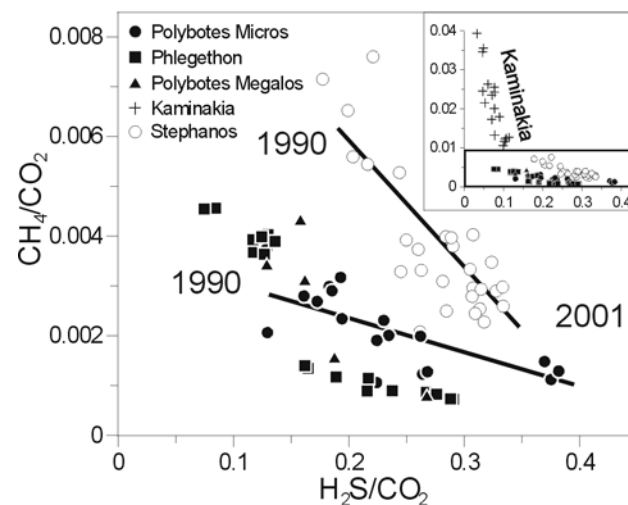


Figure 3. Diagram of CH_4/CO_2 vs H_2S/CO_2 for the Stephanos fumaroles and the Lofos dome vents (Polybotes Micros, Phlegethon, and Polybotes Megalos). In the small inlet they are plotted together with Kaminakia fumaroles.

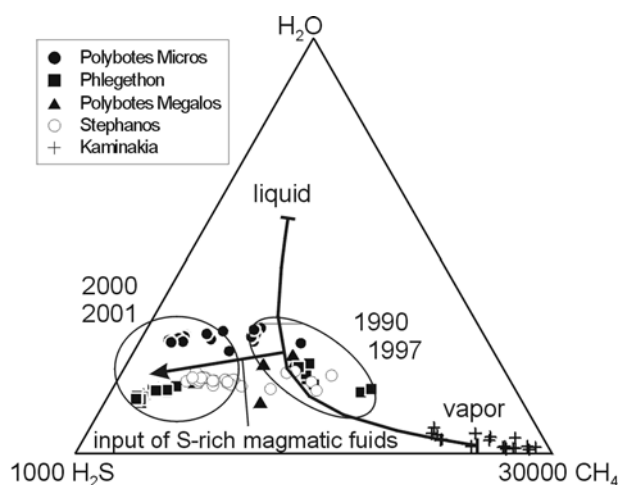


Figure 4. Triangular diagram of $\text{H}_2\text{O}-\text{H}_2\text{S}-\text{CH}_4$. See the text for the explanation of the boiling curve.

H_2S would be directly related to the relatively high contents of sulfur species, mainly SO_2 and H_2S , in the magmatic component. Methane would decrease, instead, because of the low CH_4 contents of magmatic fluids and the occurrence of redox reactions favored by the input of relatively oxidizing magmatic gases. In the triangular diagram $\text{H}_2\text{O}-\text{H}_2\text{S}-\text{CH}_4$ (Figure 4), fumarole compositions are compared with a theoretical boiling curve computed by assuming that the liquid phase is in equilibrium at 300°C with a pure vapor phase of composition similar to that measured at Kaminakia, i.e. richest in sparingly soluble gases. The boiling curve shows the compositions of the vapors separated from the liquid in a single-step process at different separation temperatures. The vapor-liquid distribution coefficients for a 2 m NaCl solution [Chiodini *et al.*, 2001] were used, in order to consider the presence of saline brines in the Nisyros hydrothermal system (liquids of Nis-1 well had up to 81,500 mg/kg Cl). Even though the resulting theoretical boiling curve represents only one of the many possible boiling paths for the Nisyros hydrothermal system, it will be used as a reference in the following discussion. Figure 4 shows that the compositions of the fumaroles sampled before and during 1997 can be explained by simple boiling of a unique liquid, while the samples collected in 2000–2001 deviate significantly from the theoretical boiling curve towards H_2S -rich compositions. This agrees with the hypothesis of an increased input of S-rich, oxidizing magmatic gas, being responsible of the observed decrease in the CH_4/CO_2 ratio and increase in the $\text{H}_2\text{S}/\text{CO}_2$ ratio.

[12] At Nisyros, CH_4 is the only reduced species, which has decreased over time; H_2 and CO remained constant or even increased, such as in Lofos dome fumaroles (H_2) and S and PP fumaroles (CO, Figure 2). There are at least two reasons explaining the different behavior of CH_4 with respect to H_2 and CO: (i) CO and H_2 are less affected by changes in redox conditions than CH_4 and (ii) CO and H_2 fugacities are mainly controlled by temperature [Chiodini and Marini, 1998]. The observed increase of H_2 and CO with time could be related to increasing temperature at depth, in support of the idea of a greater magmatic input. This aspect can be tested by applying different gas-geothermometers.

[13] One of these is the H_2 -Ar geoinicator of Giggenbach [1991], recalibrated by Chiodini *et al.* [2001] for saline brines (2 m NaCl). It gives temperatures between 350°C and 420°C , with an average of 380°C . However, these values likely overestimate the temperatures of the Nisyros hydrothermal reservoir, even of its deepest parts reached by the geothermal wells. The H_2 -Ar geoinicator is based, in fact, on the strong temperature dependence of hydrogen fugacity and on the assumption that the Ar content of hydrothermal fluids is equal to that of air-saturated groundwater

(ASG). Obviously, vapors separated through boiling are expected to have Ar/ H_2O ratios higher than that of the original liquid, i.e., higher than the ASG ratio of 2.6×10^{-7} . However, most PP and S fumaroles have Ar/ H_2O ratios as low as 8×10^{-8} , i.e., significantly lower than ASG. Excluding the occurrence of important condensation processes at PP and S fumaroles [Brombach, 2000], these low Ar/ H_2O ratios suggest that the Ar content of the hydrothermal reservoir liquid may have decreased through boiling. As a consequence the H_2 -Ar geothermometer provides temperatures higher than the real ones. Assuming, for example, an Ar/ H_2O ratio of one order of magnitude lower than that of ASG for the original liquid phase, temperatures of 280°C to 350°C , with an average value of $\sim 320^\circ\text{C}$, would be estimated. In spite of these uncertainties, there is little doubt that the observed increases in the H_2 content of Lofos fumaroles (PP, PH, PG) are due to an increase in temperature in the zones where H_2 equilibrates.

[14] Another geothermometric evaluation is possible from the $\text{H}_2\text{O}-\text{H}_2-\text{CO}_2-\text{CH}_4-\text{CO}$ gas system [Chiodini and Marini, 1998]. This CO-based graphic geothermometer indicates lower apparent equilibrium temperatures, ranging between 180 and 320°C , but clustering between 200 and 260°C (Figure 5a). These temperatures are lower than those measured in geothermal wells Nis-1 and Nis-2, suggesting that CO re-equilibrates in the separated vapor phase under the lower temperatures met by fumarolic gases in intermediate reservoir(s) along their upflow pathways. As a matter of fact, CO was recognized to be a gas species which re-adjusts quickly in response to temperature changes in high temperature volcanic fumaroles, both at White Island [Giggenbach, 1987] and Vulcano crater [Chiodini *et al.*, 1993b]. In Figure 5a, the fumaroles of Stephanos and those of the Lofos dome area lie along two slightly different trends, which can be explained by re-equilibration of CO

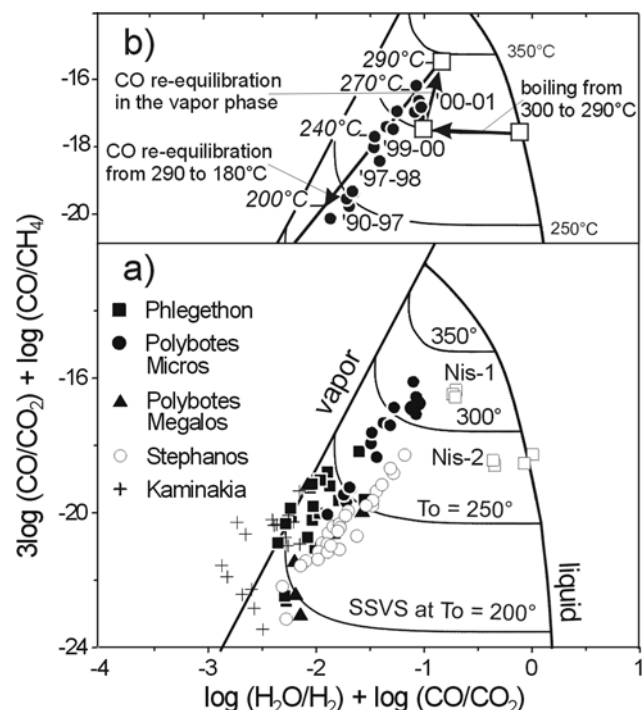


Figure 5. Plot of $3 \log (\text{CO}/\text{CO}_2) + \log (\text{CO}/\text{CH}_4)$ vs. $\log (\text{H}_2\text{O}/\text{H}_2) + \log (\text{CO}/\text{CO}_2)$ [from Chiodini and Marini, 1998]. (a) The equilibrium values in a single saturated vapor phase and in a single saturated liquid phase for different temperatures To are given by the vapor line and liquid line, respectively. The SSVS curves refer to iso-enthalpic single-step vapor separation, at different separation temperatures, from a single liquid phase of initial (equilibrium) temperature To. Squares indicate well samples. (b) Detail of the time dependent trend of PP samples (see text for details).

in the vapor phase upon cooling at nearly constant concentrations of H₂O, H₂, CO₂, and CH₄. This hypothesis is investigated in Figure 5b, where only the data of PP fumaroles are plotted. To reproduce the time-dependent trend observed for these fumaroles, the vapor phase was separated in a single step at 290°C from the liquid phase with initial temperature of 300°C and the CO content was subsequently re-equilibrated at temperatures between 290°C and 180°C. In this model, the trend depicted by the PP fumaroles is best explained by an increase in the re-equilibration temperature from 210°C, in 1990–1997, to temperatures as high as 270°C, after the 1996–97 seismic crisis (1997–2001). A similar increase in re-equilibration temperatures was inferred for the most recent samples collected from Stephanos crater fumaroles. Two possible processes may explain such time-dependent trends: (1) a decreasing transit time of gases from the deep hydrothermal reservoir to their surface discharge and/or (2) heating up of the upflow channels or the intermediate reservoirs.

[15] Summing up, the increases in CO and H₂ of most Lofos dome fumaroles suggest a localized temperature increment in the upper parts of the hydrothermal system. The absence of similar indications in other areas suggests that no general heating and pressurization took place upon input of magmatic fluids. It seems that the magmatic heat input was largely buffered by the hydrothermal system, but this speculation cannot be substantiated by a heat balance due to lack of data.

4. Conclusions

[16] Historical reports indicate that the 1873 hydrothermal eruption of Nisyros was triggered by seismic shocks. At present, no similar eruptions have yet occurred after the strong seismic crisis, which affected the island in 1996–1997. However, increasing H₂S/CO₂ ratios and decreasing CH₄/CO₂ ratios were observed for Nisyros fumaroles in 1997–2001, after the seismic crisis. These important chemical changes are interpreted as being controlled by an increasing contribution of sulfur-rich, oxidizing magmatic fluids into the hydrothermal system. This process was probably permitted by fracture opening at depth by the 1996–97 earthquakes. Increments in H₂ and CO suggest the local increases in temperature and pressure in the upper parts of the hydrothermal system. However, heating and pressurization is not a general process, probably due to the buffering role of the hydrothermal system. Nevertheless, the 'hydrothermal' hazard is higher at present than in the 90's. Indeed, the chemical changes are accompanied by micro earthquake activity and ground deformations [Lagios *et al.*, 2001, Osservatorio Vesuviano unpublished data].

[17] The historical hydrothermal eruptions, the present chemical changes of the fumaroles and the physical phenomena affecting Nisyros could represent long-term precursors of a new period of volcanic unrest, which might culminate in a magmatic eruptive phase. Similar phenomena actually preceded recent magmatic eruptions such as at Montserrat, Lesser Antilles [Chiodini *et al.*, 1996; Hammouya *et al.*, 1997] and Guagua Pichincha, Ecuador [Marini *et al.*, 1991].

[18] **Acknowledgments.** This work was financially supported by EU (GEOWARN Project IST 1999–12310) and by GNV-INGV (Volcanology

National Group of Italy). We wish to thank Patrick Allard for his constructive comments.

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