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# GEOCHEMICAL ASSESSMENT OF THE THERMAL FLUIDS EMERGING ALONG THE AEGEAN VOLCANIC ARC (GREECE)

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## ABSTRACT

Aegean volcanic arc developed during Quaternary time as a result of a lithosphere subduction process. Starting from Soussaki-Loutraki and Methana thermal areas, located in the Peloponnese peninsula, the arc proceeds through Aegina, Milos and Santorini islands, to reach, in the south-eastern part, Kos and Nisyros islands. Volcanic activities are still well pronounced at Nisyros in form of seismic activity, of craters of very recent hydrothermal explosions, hot fumaroles and thermal springs, but these surface manifestations tend to decrease moving to the north-western part of the arc.
Isotopic and chemical analyses were performed on water and gas samples collected in different areas of the volcanic arc and compared with the literature data, in order to attempt the assessment of the thermal fluids emerging in these volcanic structures. H, O and C stable isotopes, coupled with the major chemistry, have been used to evaluate the origin of the main components of the fluids such as $H_2O$, $CO_2$, $H_2$, $CH_4$, $N_2$; reservoir temperatures were derived by solute concentrations, and by isotopic fractionations in the ($H_2$-$H_2O$), ($CO_2$-$CH_4$) and ($H_2$-$CH_4$) pairs. Chemical solute concentrations and isotopic composition of waters were interpreted in terms of mixing and subsurface boiling processes, involving cold meteoric waters as well as hydrothermal and seawaters. Gas geochemistry reveals that input of magmatic fluids must be taken into consideration in the highest temperatures environments. Methana, Aegina, Kos and, partially Soussaki-Loutraki areas likely represent geothermal systems in their waning stage, while surface fluids of Santorini, Milos and Nisyros reflect the existence of still active geothermal systems.

## 1. INTRODUCTION

The Aegean area is one of the most rapidly deforming parts of the Alpine-Himalayan mountain belt (Figure 1).
Since Oligocene volcanic activity was constantly present in the Aegean area. The first voluminous volcanic activity was manifested during Oligocene in north Greece; subsequently it migrated south-westward through the north Aegean islands (voluminous Early Miocene volcanism) and Cyclades (Miocene I-type plutonism) to a restricted belt which extends from Soussaki area, to Nisyros island, to form the so-called South Aegean Volcanic Arc (SAVA). In the Aegean Sea this arc represents the youngest example of volcanism, and the only one that can be related, in age and in position, to the present zone of subduction. The products of this volcanism form a typical calc-alkaline association which displays an evolution from basalts to rhyolites. Their chemical characteristics are closely comparable with those of volcanics of island arcs sited on thin continental margin (Fyticas *et al.* 1984).
There are some significant variations along the SAVA, both in magmatic character and in mode of eruption: in the western sector the volcanic centers are dominated by the presence of domes and lava flows with subordinate pyroclastics. The central and eastern sectors of the arc are dominated by large central volcanoes often characterized by summit calderas.
Actually, volcanic activity along the SAVA is restricted to argillification processes, acid leaching, fumarole deposits etc, in the north western sector of the arc. In the western sector, Nisyros experienced last eruption during May 1983, and four periods of eruption took place at Santorini in only 25 years during this century, from 1925 to 1950.
Heat content being equal, the size of the hydrothermal manifestations depends on the quantity of the water available and on the characteristics of the cover series, apart from the circulation networks created by the disjunctive tectonics. Considering the entire geological situation on the arc, the factors which have favored the formation of huge hydrothermal alterations are mainly the availability of both water and fissures.

The aim of this paper is essentially directed to underline the geochemical features of the thermal fluids emerging in different volcanological contexts, represented by the several volcanic centers constituting the SAVA. Environmental isotopes and major chemistry have been used to describe the interactions between surface meteoric water, seawater and deep fluids of hydrothermal/volcanic origin.

## 2. RESULTS

Meteoric waters, cold mineral waters, thermal waters from spring , shallow and deep boreholes, fumaroles and dry gas manifestations constitute the sources of chemical and isotopic data. Analyses came either from field activity sponsored by IAEA (i.e. Sousaki-Loutraki, Methana, Aegina, Milos, Kos and Nisyros) and Chiodini *et al.*(1994; i.e. Santorini island). Data reported by Liakopoulos *et al.* (1991), Minissale *et al.* (1997) are also taken into account for this general review on the SAVA. Sets of analytical results for quite arbitrarily selected water and gas samples, spanning the whole range of the tectonic, geological and hydrological environments of the SAVA are used in the following discussion.

### 2.1 The origin of thermal waters

Early observations that the deuterium contents of most geothermal water discharges is very similar to those of local groundwater suggested a predominantly local, or at least nearby, meteoric origin of thermal fluids . Recent findings, however, point to a wider range of source components. Investigations into the origins of these waters are also complicated by a number of secondary processes affecting the isotopic compositions of deep waters during their passage to the surface. The three generally accepted major processes, to be taken into consideration are: i) isotopic exchange of oxygen-18 with rock; ii) mixing of waters of different origin, and iii) boiling and associated vapor separation. Because the rate of $^{18}O$-exchange between water and rock decreases rapidly with temperature, the presence of an $^{18}O$ shift in neutral chloride waters is usually taken as a good indication for the present or former existence of reasonably high temperatures (>200°C) within the geothermal system under investigation.

In the islands, marine waters might enter the aquifers trough different pathways, e.g. direct seawater ingression, particularly near the coastal zones, atmospheric transport of marine spray, uprising of comparatively deep waters coming from geothermal aquifers fed, at least in part, by seawater. The plot of Figure 2a shows a well-defined mixing line that extends from the composition of local meteoric waters and seawater, confirming the important role play out from the sea in the fluids emerging in the whole volcanic arc.

The quite close position on the thermal waters at Soussaki-Loutraki, Methana, Santorini, Kos and Nisyros, to that of seawater, far from that of local groundwater may be taken to indicate a derivation from somewhat modified seawater. For example, water sample SL1 shows sensible depletion in D content and contemporaneously an enrichment in Cl concentration with respect to the actual seawater (Figures 2a and 2b). A possible explanation requires that boiling processes are involved to modify the composition of the original water that is likely represented by a mixed water between seawater and meteoric water (point A, in the inbox of Figure 2). Single step steam separation at dept from a mixed water (A) at initial temperature of 160°C (inferred by K-Mg geothermometer, see below) and a separation temperature of 80°C (measured at surface in the fumarolic fluids), produce, after a steam loss, a residual water (B). When water sample (B) approach the surface, it may undergo to an evaporation at a constant temperature of about 80°C and a 20% of steam loss. This produce a kinetic fractionation effect on the water samples with an enrichment of about 10‰ and 3.5‰ in D and $^{18}O$ respectively (point C, in Fig. 2). Sample (C) shows an isotopic composition, which coincides with SL1 thermal water. The 'salt effect' on the isotopic fractionation of the evaporating saline waters has been neglected in the calculations.

Water samples 15 and 27 at Milos island are enriched of 5 to 6 ‰ in $^{18}O$ with respect to seawater, while D contents remain practically the same. This oxygen shift may be attributed to a certain water/rock isotopic exchange at high temperature, similarly to the marine intrusion observed at Vulcano island in the Aeolinan Volcanic Arc in the Mediterranean Sea (Panichi and Noto, 1992). However strong differences in the salt contents of these exchanged geothermal waters occur, being the Milos hydrothermal fluids diluted with respect to seawater (about 10 g/l; Figure 2b), while high enthalpy fluids are characterized by very high Cl contents (about 50 g/l in the NIS2; Geotermica Italiana,1983, and 58 g/kg at MILOS2; Minissale *et al.*, 1997). Hot fluids delivered by the geothermal wells show similar $^{18}O$ enrichments but about 10‰ depletion in D contents. These two different patterns are not yet completely understood, but one possible explanation provide that leaching of evaporite rocks of marine-modified waters followed by extensive evaporation of the resulting brines occurs in the deep horizons of the islands. The reservoir waters of marine origin at Milos are locally submitted to a mixing with deep waters of different origin and characterized by lower Cl contents. Milos 15 and 27 samples both emerging in the eastern sector of the island, may be the result of an initial exchange with rock of the seawater that determine the increasing of $^{18}O$ and solute contents followed by an admixture with magmatic fluids. The magmatic component is believed to be depleted of 10 to 30 ‰ in D and enriched of 6 to 9 ‰ in $^{18}O$ and contains 15 to 20 g/kg of Cl (Giggenbach,1992). However, partial addition of this water to the brine seems unable to completely explain the actual chemical and isotopic composition of Milos water sample, being the Cl contents lower than that the diluted end-member of the hypothetical mixture. Addition of low-Cl fluids must be considered; coming either from infiltration of meteoric waters into the geothermal reservoir, or from a steam phase derived from boiling processes of the geothermal brine itself. No direct evidences have been reached in favor or in contrast with these hypotheses.

The presence of uprising vapor from high temperature reservoirs at Nisyros and Santorini results from the isotopic characteristics of the fumaroles emerging in those island. High temperature fumaroles are so present in the Milos island, but they have an isotopic composition of –12 and –80 ‰ in $^{18}O$ and D respectively, and seem to be unable to represent any suitable product of evaporation processes involving deep geothermal waters.

The isotopic composition of the fumarolic steam varies in the different islands, and sometimes in the same island as in Nisyros (see samples N13-14 and N15-16 ). Their isotopic compositions have been interpreted as derived by single step steam separation processes occurring at depth inside shallow and/or deep aquifers, which are present in the Santorini and Nisyros volcanic systems. At Nisyros, DGB and SGW represent the parent waters from which the different steam samples may derive, assuming the initial temperature being 330° (measured in the geothermal well; Geotermica Italiana, 1983) and 175°C (evaluated by solute geothermometers) for the geothermal brine and the shallow groundwater respectively. In the case of Santorini 40, essentially constituted by the actual seawater, may conveniently represent the parent water for steam samples NK1-2, when an evaporation from reservoir temperature of 275°C (inferred by gas geothermometry) to the surface temperature of fumaroles are considered.

Points off the mixing line may indicate analytical error or a third fluid component. Combining the information from diagrams (a) and (b) of Figure 2, addition of deep steam to shallow groundwater partially mixed with local seawater may account for the Cl, D and $^{18}O$ contents of waters from Milos (ML26), Santorini (S1), Nisyros (N1) and Soussaki-Loutraki (SL15) geothermal areas.

Finally, water samples having δD values more negative than –30 ‰ may represent the local meteoric waters of different volcanic centers of the SAVA. Changes in the isotopic composition of these waters may be related, as a first approximation, to differences in the mean annual composition of rain water in each area. However, inspection of Figure 2b may suggests that each sample may be modified by addition of deeper steam.

The addition of deep fluid of geothermal or volcanic origin to groundwaters may produce brackish solutions where Cl or $SO_4$ or $HCO_3$ are the dominant ions, as a function of the relative amount of the HCl, $SO_2/H_2S$ and $CO_2$ in the uprising gases. Inspection of Figure 3, where the relative concentrations of the three major anions are reported, indicates that groundwaters having TDS values as high as 2.5 g/l show a variability that is due to addition either $CO_2$-rich or HCl-rich gas mixtures. Water sample Santorini-19 contains relatively higher sulfur compounds in solutions, that, nevertheless, remain lower than 20% of total anions in these group of groundwaters. Water samples which are influenced by seawater show TDS values ranging from 6 to 44 g/kg for little modified seawater (SL1), and reaching 83 g/kg in the case high temperature geothermal brine (NIS2) and 113 g/kg in the MILOS2 water. Most of these samples form a cluster around seawater point, part of those occupying the "mature waters" area, as defined by Giggenbach (1991) for water flowing in the volcanic environment.

### 2.2 Solute geothermometry

Most ionic solutes geothermometers give suitable results if used with close to neutral waters containing chloride as the major anion. Considering the indications obtained by the Fig.3 only water samples from NIS2, MILOS2, Milos-27, SL1 and SL2 fall in the compositional area marked "mature waters". For these Cl-rich waters application of Na-k, Na-K-Ca and K-Mg-geothermometers becomes useful. On the other hand, great care should be taken in the interpretation of the temperatures

suggested by all other data points. By combining two sub-systems involving the Na-feldspar/K-feldspar and K-feldspar/chlorite temperature dependence reactions, Giggenbach (1988) proposed a method allowing the degree of attainment of water-rock equilibrium to be assessed and unsuitable samples to be eliminated.
Figure 4 shows the evaluation of the Na-K-Mg temperatures of the selected samples of the SAVA reported in Fig.1. Geothermal well discharges (NIS2 and MILOS2) plot, as expected, close to the full equilibrium at their deep temperature. Corresponding shallow-well and spring waters are all shifted, to a varying degrees, towards the Mg corner. Their position indicate only minor drops in the Na-K-Temperatures but major decreases in the K-Mg-temperatures. This trend reflects the much greater speed with which the latter geothermometer adjusts to a change in temperature as compared to the system. The Milos water samples 27-26 and 35 Na-K show a very large shift along the straight line that describes a constant ratio Na/k = 3.2. This may be due either to a continuous evolution trend of these waters by interaction of "immature waters" towards a full equilibrium condition in an aquifer (MILOS2) characterized by a temperature of 320$^{o}$C. Alternatively, different steps of mixing between a deep geothermal water and shallow groundwater relatively enriched in Mg ions may be considered. Looking at Fig.3, the isotopic composition of these Milos waters describe a straight line that joints a meteoric component (35) with modified seawater (15 and 27), suggesting that mixing between these two components is the candidate mechanism to explain the observed values.
Figure 4 shows a set of samples, represented by Methana-1,3, Kos-1, Santorini-40, Nisyros-12, which may be considered seawater driven geothermal systems without any significant deviation from the point marked SW. In this case the effects of thermal processes may be hardly assessed.
Addition of $CO_2$-rich or quite acid fluids to groundwater place it in the compositional area marked "immature waters" and no realistic K-Mg-temperatures may be derived.

## 3. THE ORIGIN OF THE GAS MIXTURES

The data on gas mixtures from SAVA are by no means exhausted here. The samples represent the general situation and are the best compromise between geological setting, temperature gradients, gas production, area accessibility, etc.
Chemical data on gas samples derived from thermal springs, steaming ground, fumaroles and geothermal deep wells, are reported on a water-free base in Figures 5 and 6. Most of gas sampled are essentially made up of $CO_2$, which is followed by $N_2$ and $O_2$. Because of the low pressure of steaming grounds at Milos, Santyorini and Sousaki-Loutraki and morphological constrains, variable mixing with air takes place in those sites. The $N_2/(O_2+Ar)$ ratio is, sometime, slightly higher than the atmospheric value (3.57) as due by either different dissolution of $O_2$ and $N_2$ in water (steam condensates) and/or consumption of $O_2$ in oxidation processes involving the rock matrix and/or gas constituents. Minor constituents ($CH_4$, $H_2$, $H_2S$ and CO) are present in variable proportions, reflecting different extents of addition of air to a $CO_2$-rich end-member. However, the $CH_4/CO_2$ and $H_2/CO_2$ ratios of the $CO_2$-rich end-member are not significantly alterated by addition of air.
Because of the ubiquitous presence of seawater in the thermal aquifers of the volcanic arc, interaction between seawater and uprising steam will produce some effects on the composition of the surface gas manifestations. "One box model" simulation indicate that the seawater-steam interaction produce enrichment of the $N_2$ contents of the free gas leaving the solution, while smooth trends are observed for $CO_2$, $CH_4$, CO and $H_2$ (Chiodini et al,1994). From these observations it can be concluded that the steam interacting with seawater should not differ significantly from the gases separating from it at least in relative $CO_2$-CO-$CH_4$-$H_2$ concentrations.
However the occurrence of biological removal of H2 during gas bubbling through seawater is suggested by the large fluctuation in H2 content. Similarly, H2S concentrations are often below the detection limit or slight above, except for Nisyros gas samples and the gas phase delivered by the Milos geothermal well. The lack in the gases discharged by the springs suggests oxidation and/or solution before emergence.
The origin of carbon dioxide can be investigated by comparing the carbon isotopic composition of the manifestations of the SAVA with literature data. $\delta\ ^{13}C(CO_2)$ mean values are -0.1± 0.4 ‰, -2.2± 0.5 ‰, -3.4± 0.2 ‰ and –3.45 ‰ at Santorini, Nisyros, Milos and Methana respectively. These results evidence deep $CO_2$ in the SAVA with a more positive $\delta^{13}C$ value than those typically obtained for mantle-magmatic carbon (from -4 to -8‰). Deep $CO_2$ characterized by a $\delta^{13}C$= -3 ‰ or more positive can be attributed to a mixed magmatic-sedimentary origin only if isotopic fractionation during uprising and interaction of the gases with reservoir rocks can be excluded. At present, we are unable to define the actual mechanism of contamination of the magmatic carbon dioxide by sedimentary rocks. The foregoing observations regarding the extensive water/rock interactions of deep fluids at Nisyros and Milos, and relatively high $^{3}He/^{4}He$ ratios (3.5 Ra, at Santorini; Chidini et al, 1994) seem to argue in favor of direct contamination of the magmatic source by sedimentary carbon.

### 3.1 Gas geothermometry and geobarometry

Two different theoretical models can be taken into account in order to evaluate the thermodynamic conditions of the gas mixtures in the zones where gas constituents probably equilibrate.

Overall equilibrium among gases

This theoretical model considers that overall equilibrium is obtained among gas constituents in the $H_2O$-$CO_2$-$CH_4$-$H_2$-CO system (Bertrami *et al.* 1985). The diagram of Figure 7 considers that the gas species equilibrate in the "pure" vapor phase. In this model the $H_2$/CO ratio practically depends upon $P_{CO2}$ only while log ($CO^4$/ $CH4*CO_2^3$) is fixed by the equilibrium temperature of the reaction involving those components and the $H_2O$. Under these assumptions gas mixtures from different localities indicate apparent equilibrium temperatures in the range 170–320 $^{o}$C. The lowest temperatures have been found in Kos, and the highest in Santorini, Milos and Nisyros. Equilibrium $P_{CO2}$ values are lower than 1 bar at Kos and the shallow hydrothermal systems at Nisyros, but increases up to about 10 bars at Milos, NIS2-well, Santorini and Sousaki-Loutraki. Some values from Santorini are in excess of some tens of bars, eventhough the lowest values are the most likely ones (less affected by interaction with seawater). Temperature indication for the SL fluids appear to be exceptionally high in respect to the indications from chemical and isotopic evidences of waters samples, and this discrepancy may be overcome if we assume that log ($H_2$/CO) is increased by removal of $H_2$ upon massive interaction in the seawater.

Redox conditions buffered by gas-rock equilibria.

The second theoretical model assume that redox conditions in the gas equilibration zone are buffered by gas-rock equilibria, according to the hydrothermal FeO-$FeO_{1.5}$ rock buffer by Giggenbach (1987). Gas samples from Santorini, Sousaki-Loutraki and Kos appear to memorize redox conditions more oxidizing than expected in "typical hydrothermal systems (Figure 8). They, indeed, result shifted at lower $CH_4/CO_2$ ratios,

towards the $SO_2$-$H_2S$ magmatic. gas buffer by Giggenbach (1987), as a consequence of an input of magmatic gases in some part of the hydrothermal systems, even if no $SO_2$ has been detected in the surface fluids of those areas. However, sulfur compounds are largely present in the alteration minerals of the thermal areas of those islands.

Isotope gas equilibria

The $CO_2$, $CH_4$ and $H_2$ gas components at Nisyros were separated and analysed for their isotopic composition. Carbon isotopes show an almost constant content of both $CO_2$ (average value –2.3 ± 0.4‰) and $CH_4$ (average value –22.2 ± 0.5‰), while $H_2$ in the low-temperature fumaroles results depleted by 70‰ of the D content with respect to the high-temperature group (-540 ± 2‰). Deuterium content of condensed steam also varies considerably in the two groups of fumaroles characterised by –10.5 ± 2.5‰ and –42 ± 1.1‰ values. Nearly homogeneous temperatures result for all the fumaroles analysed for carbon isotope equilibration between $CO_2$ and $CH_4$. An average value of 368 ± 12°C was obtained, which is not far from the maximum values measured in the NIS2 and MILOS2 wells. When the pairs $CH_4$–$H_2$ and $H_2O$–$H_2$ are considered, the temperatures at which hydrogen isotope equilibrium is attained are considerably lower than those computed through carbon isotopes, because kinetic reactions are different, and CH4-CO2 is "frozen" at higher temperatures.
These values are pointing (as is usual for reactions involving $H_2$) either to the lack of equilibrium or equilibration at considerably lower and superficial temperatures e at shallow levels. Based on observations in volcanic gases (Giggenbach, 1987) and geothermal fluids (Panichi and Noto 1992), $H_2$ should be one of the species that responds most rapidly to changes in equilibrium conditions of the rising vapours.

## 5. CONCLUSIVE REMARKS

The nature of the surface manifestations and the isotopic and chemical composition of the fluids sampled from many discharge points on the western sector of SAVA (Soussaki-Loutraki, Aegina, Methana) and at Kos island on the eastern sector, are typical of geothermal systems in their waning stages. The existence of elementary S in zones of extensive rock alterations is compelling evidence for the occurrence of a previously more intense geothermal activity. During this early period the underground hydrology of the area is likely to have been dominated by the rise of geothermal fluids occupying a considerable part of available fluid spaces. As geothermal activity receded, meteoric waters and seawater invaded these systems, largely obliterating near-surface expressions of the thermality. The major indications of the persisting presence or production of geothermal fluids are the strong-to-moderate gas discharges associated with the manifestations with reservoir temperatures lower than 160°C.
Depending on the degree to which cooler meteoric waters were able to penetrate the spaces formerly occupied by geothermal fluids, more or less extensive, stagnant, possibly sealed-off pockets of such high-temperature phases may still persist at depth. The only indication of the presence of these pockets may be the leakage of gas-rich phases, or the establishment of a thermal "halo" around the reservoir of the hot fluid. The interaction of the $CO_2$ released with meteoric waters, or intruded seawater, however, leads to the formation of highly aggressive waters and rock-water interaction characterised by quantitative leaching of cations and partial re-equilibration processes. Under these circumstances any information carried by the waters from deeper levels is erased.
On the contrary, water and gas samples from Milos, Santorini and Nisyros islands, all belonging to the eastern sector of the SAVA, clearly indicate the actual presence of still active high enthalpy geothermal systems. These differences can be accounted for the effect of the difference in lithospheric stress-fields existing in the two sectors of the arc: in the western sector there is a less marked extensional regime, making it more difficult for magmas to rise, thus favoring deeper fractionation. In central and eastern part a strong tensional tectonic regime favor the rise of basic magmas and the formation of vast shallow magma chambers (Fytikas *et al.*1984). Finally, andesitic water may be considered as an effective components of the hydrothermal solutions at Milos, i.e. in correspondence of 'suture' zone of the two microplates that constitute the Southern Aegean Volcanic Arc.

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# REFERENCES

Bertrami, R., Cioni, R., Corazza, E., D'Amore, F. and Marini, L. (1985). Carbon monoxide in geothermal gases. Reservoir temperature calculations at Larderello (Italy). *Geothermal Res. Counc., Trans*., Vol.9, pp. 299-303.

Chiodini G., Cioni R., Dotsika E., Fytikas M., Leonis C., Magro G., Matini L., Michelot J.L., Raco B., Taddeucci G. (1994). Fluid geochemistry for the volcanic surveillance of Thera Island. In: *Proceedings of International workshop on European Laboratory Volcanoes*, Aci Castello (Catania), pp.18-21.

Fytikas, M, Innocenti, F., Manetti,P., Mazzuoli, R., Peccerilo,A. and Villari, L. (1984). Tertiary to Quaternary evolution of volcanism in the Aegean region. In: *The Geological evolution of the Eastern Mediterranean*, Geological Society of London Special Publication No. 17, pp. 687-699.

Geotermica Italiana (1983). Report for Nisyros 1 Geothermal Well. Athens, PPC-EEC, 106 pp.

Giggenbach, W.F. (1987). Redox processes governing the chemistry of fumarolic gas discharges from White Island, New Zealand. *Applied Geochemistry*, Vol. 2, pp. 143-161.

Giggenbach, W.F. (1988). Geothermal solute equilibria: derivation of Na-K-Mg-Ca geoindicators. *Geochimica et Cosmochimica Acta,* Vol. 52, pp. 2749-2765.

Giggenbach, W.F. (1992). Isotopic shift in waters from geothermal and volcanic systems along convergent plate boundaries and their origin. *Earth and Planetary Science Letters,* Vol. 113, pp. 495-510.

Liakopoulos, A., Katerinopoulos, A., Markopoulos, T. and Boulegue, J. (1991). A mineralogical petrographic and geochemical study of samples from wells in the geothermal field of Milos island (Greece). *Geothermics,* Vol. 20, pp. 237-256.

Minissale, A., Duchi, V., Kolios, N., Nocenti, M. and Verrucchi, C. (1997). Chemical patterns of thermal aquifers in the volcanic islands of the Aegean Arc, Greece. *Geothermics*, Vol. 26, pp. 501-518.

Panichi, C. and Noto, P. 1992. Isotopic and chemical composition of water, steam and gas of the natural manifestations of the island of Vulcano (Aelioan Arc, Italy), *.Acta Volcanologica*, Vol. 2, pp. 297-312.

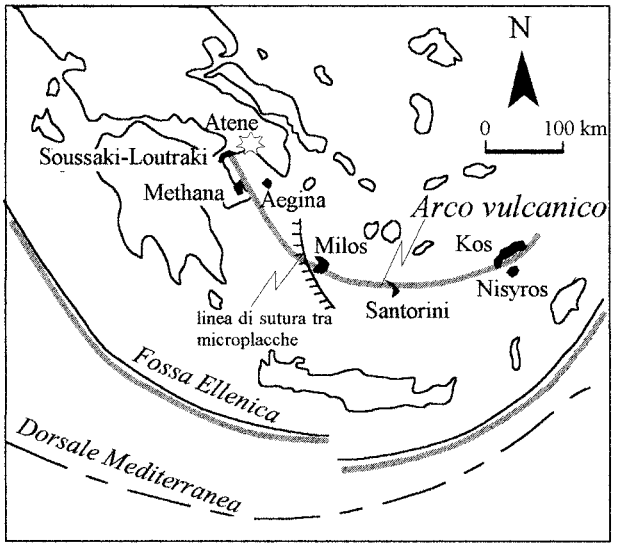


Figure 1. Sketch map of the Southern Aegean Volcanic Arc (SAVA)

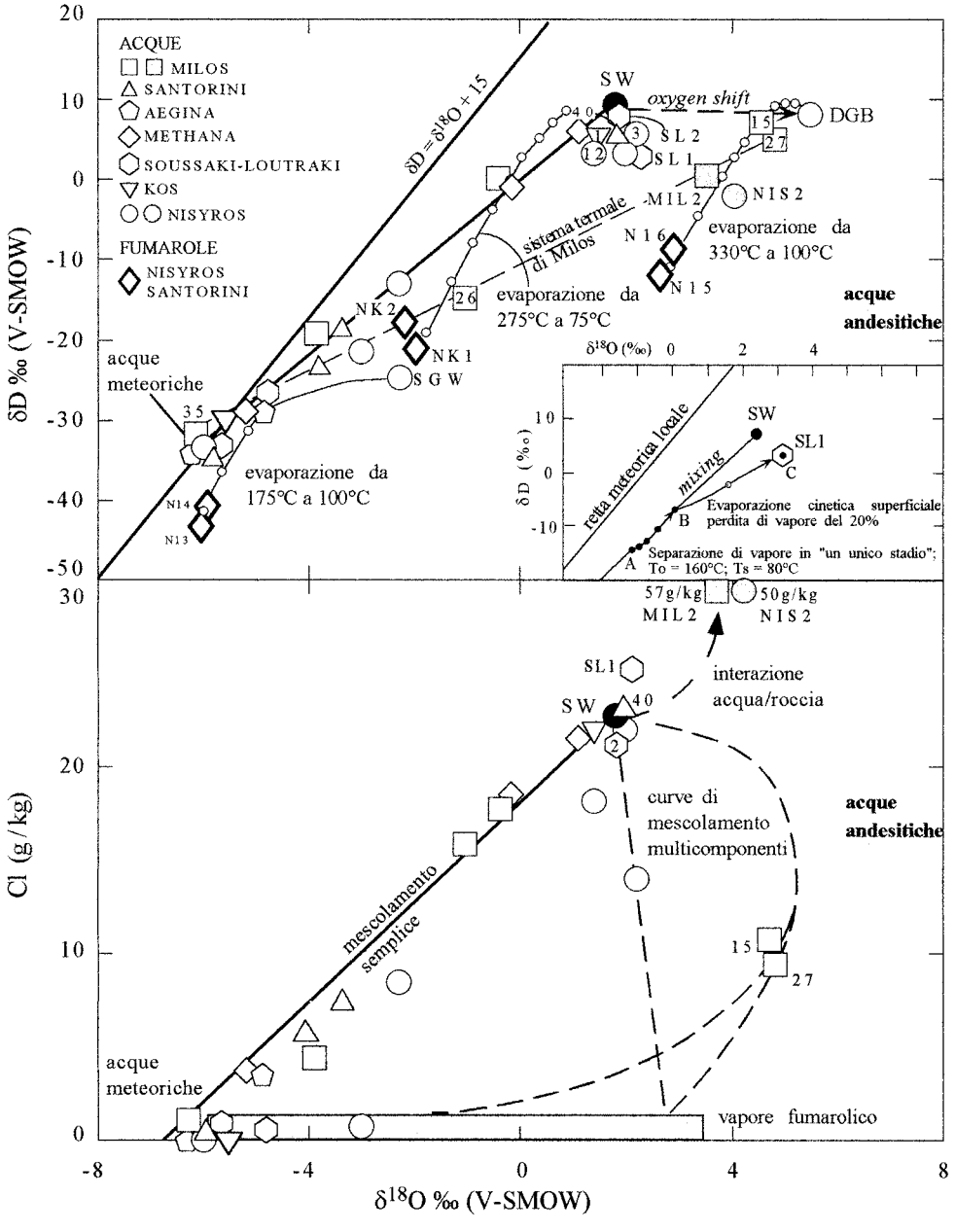


Figure 2. D, $^{18}O$ and Cl contents in selected samples from the SAVA. Mixing and evaporation processes are described.

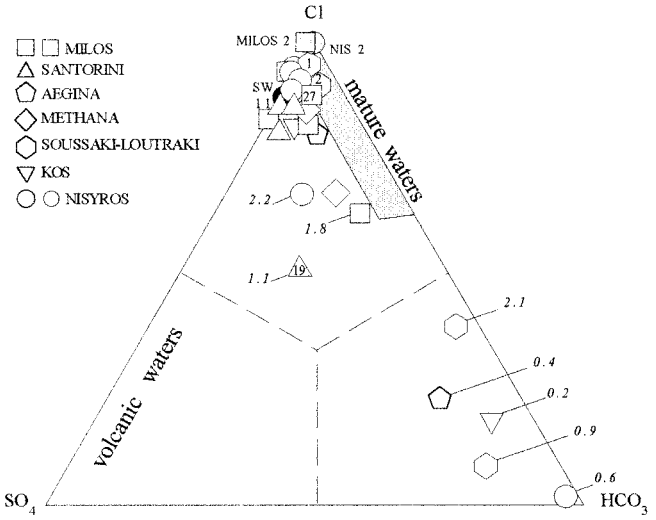


Figure 3. Cl-$HCO_3$-$SO_4$ relative concentrations of selected waters of SAVA. Italic numbers are TDS values.

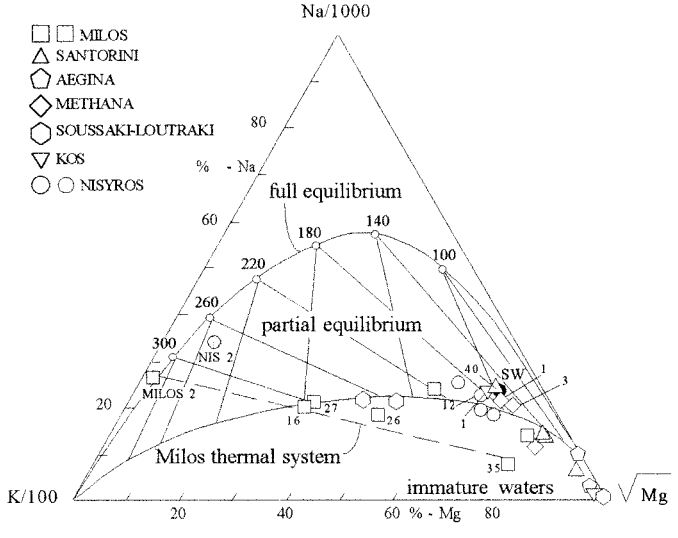


Figure 4. Na-K-Mg relative concentrations of selected waters of SAVA and inferred temperatures.

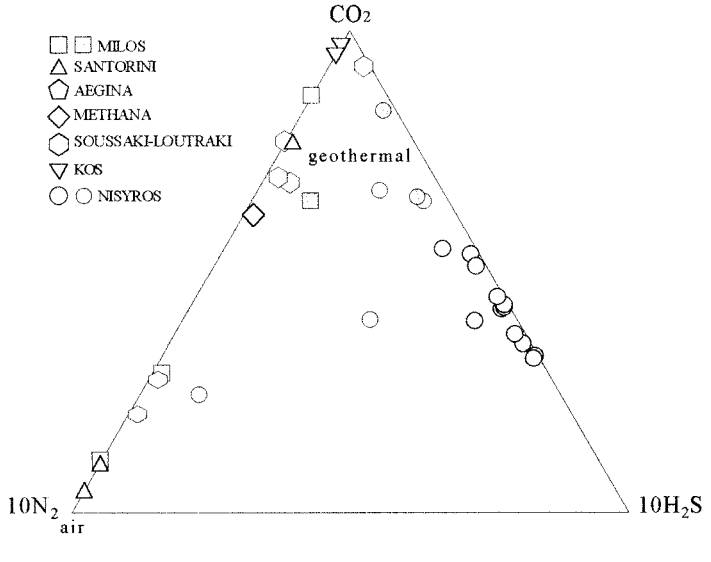


Figure 5. $CO_2$-$H_2S$-$N_2$ relative concentrations of selected waters of SAVA .Full symbols aregeothermal fluids.

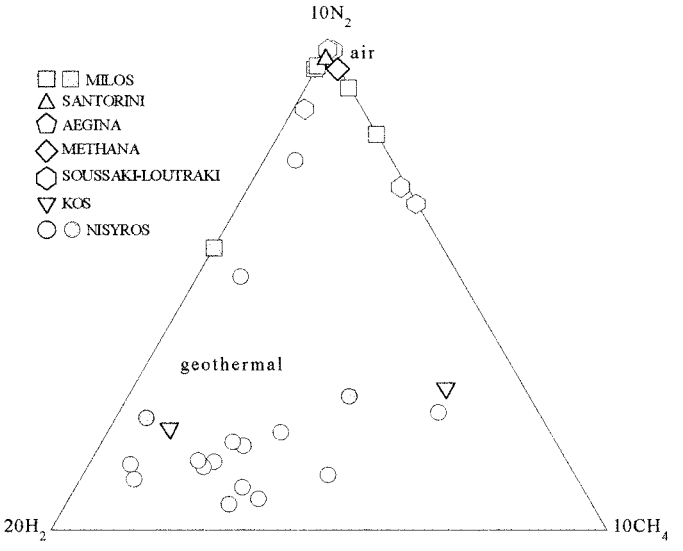


Figure 6. $N_2$-$CH_4$-$H_2$ relative concentrations of selected waters of SAVA . Full symbols are geothermal fluids.

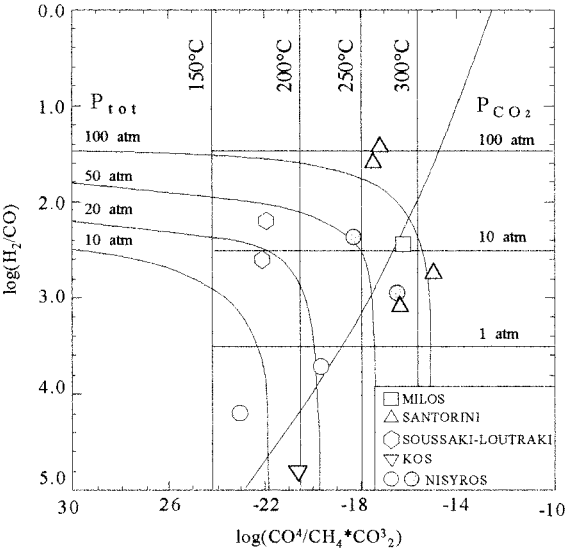


Figure 7. Log($H_2$/CO) vs. Log($CO^4/CH_4*CO_2^3$) diagram. Full symbols are geothermal fluids.

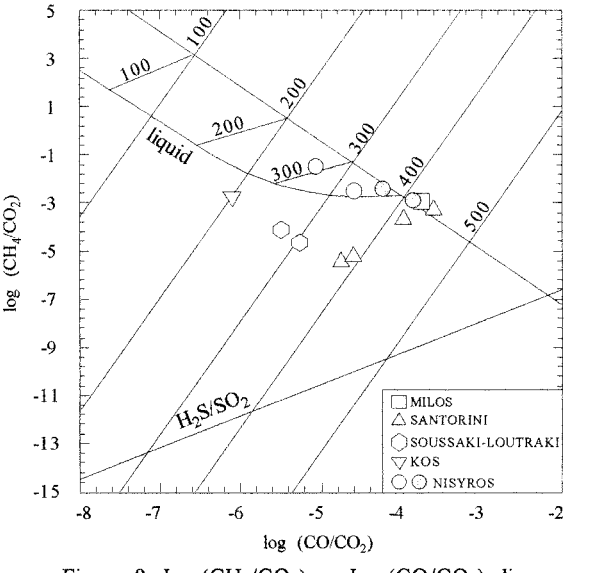


Figure 8. Log($CH_4$/$CO_2$) vs Log(CO/$CO_2$) diagram. Full symbols are geothermal fluids.