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NATURAL DEGASSING OF CARBON DIOXIDE AND HYDROGEN SULPHIDE AND ITS ENVIRONMENTAL IMPACT AT MILOS ISLAND, GREECE

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Abstract

The Aegean region represents an active convergent zone, where continental micro-plates exhibit a complex interaction between the African and the Eurasian plates. The calc-alkaline volcanic activity of the Southern Aegean region developed in various volcanic centers from Soussaki to Nisyros through Methana-Poros, Milos and Santorini. Milos Island has been an active volcano till the middle of Quaternary *and is at present characterized by a high enthalpy geothermal system. The volcanism started 3.5 Ma ago and still continues up today in the form of post-volcanic manifestations.*

Most quiescent volcanoes released large amounts of CO_2 *and* H_2S *through fumarolic activity and soil diffuse degassing. Numerous small fumaroles occur in various places, mainly at Kalamos and Adamas volcanic areas. Also along* the southern coast of the island there are volcanic gas manifestations in the sea. *Gases were sampled from fumaroles at Kalamos area as well as from north east part of Adamas village. Furthermore many soil gases were sampled at 50 cm depth and analyzed for their chemical composition. Apart from atmospheric gases (*N_2 *and* O_2*), which sometimes contaminate the samples, the main gas phase is* CO_2*. Sometimes also* H_2S*,* CH_4 *and* H_2 *are present in high amounts while CO and He are always present in trace amounts. The He isotopic composition highlights a significant mantle component.*

CO_2 *and* H_2S *concentrations higher than in the normal atmosphere can be stimulating for plant growth until certain levels and detrimental above them. As for many active geothermal areas of the world also* H_2S *and* CO_2 *concentrations measured in the area of Milos could be of concern for human health.*

Key words: *Volcanic gases, Health hazard, Environmental impact, South Aegean Volcanic Arc, Milos Island.*

1. Introduction

A volcanic gas is a relatively heterogeneous mixture, mainly dominated by steam (up to 99 % v/v), where a large number of other gas compounds are dispersed: SO_2, H_2S, HCl, HF, H_2, N_2, CO, CO_2, CH_4 and other hydrocarbons, noble gases, COS, etc. with contents that may range from ppbv or ppmv to few % v/v. The determination of gas species at low to very low concentrations is not only an analytical challenge, being some compounds in trace amounts to be considered useful indicators of impending eruptive events (e.g. Chiodini et al., 1993; Giggenbach, 1996; Delmelle & Stix, 2000). The yearly flux of carbon from sub-aerial volcanoes in volcanic arcs has been estimated at 13.5% (range of 5-25%), of the mid-ocean ridge flux of 2.1 x 10^{10} moles of carbon (Marty and Jambon, 1987).

Mörner and Etiope (2002) have recently evidenced that the contribution of geothermal systems to lithospheric carbon degassing, although at present poorly constrained, is probably higher than volcanic degassing. An accurate quantification of CO_2 and CH_4 fluxes from low-enthalpy geothermal systems would therefore add important data for the accurate quantification of their contribution to the earth's carbon budget and to the global climate change. Both gas species have in fact important greenhouse effects and prediction of future climate scenarios rely heavily on a better quantification of their fluxes between all geochemical spheres.

H_2S is a toxic gas producing multiple effects. It is colourless gas with unpleasant odour of bad eggs. In nature large amounts are produced during processes of biological decomposition. A major part of the atmospheric hydrogen sulphide is of natural geothermal origin. Air pollution is of anthropogenous type as well. Industry is the main source - coke ovens, cellulose production, artificial fibbers, natural gas and oil-product refining.

Contact of man with this gas is affected through the respiratory system. Scanty information exists on possible penetration through the digestive tract. The gas is absorbed by the organism through the lungs. In the liver and kidneys it is transformed into tiosulphates and sulphates. It is eliminated through the lungs, urine and fecal matter. Health effects are as follows - low concentrations may irritate the mucous tissues and cause conjunctivitis, and high concentrations may cause serious damages of the respiratory organs.

The aim of this paper is present the geochemical characterization of the main fumarole degassing and the soil gases of Milos Island geothermal field. Possible impact on the surrounding environment and on human health is also discussed.

2. Geological setting

The Aegean region represents an active convergent zone, where continental micro-plates exhibit a complex interaction under the influence of the overall N-S convergence between the African and the Eurasian plates. Apart from the compressional trench zone, the rest of the Aegean region is dominated by an extensional regime as evidenced by predominantly extensional fault plane and the presence of numerous normal faults (Mckenzie, 1972; Angelier et al., 1977; Dewey and Sengor, 1979). The volcanic arc lays ca. 150 km above the subduction zone, which forms an amphitheatre-like conical plane, with a maximum depth of 190 km at the central part of the South Aegean Volcanic Arc. (Spakman et al., 1988; Truffert et al., 1992; Papadopoulos et al., 1986; Papazachos, 1990), (Fig. 1).

The stratigraphy of Milos Island is composed, from the bottom to the top, by altered crystalline metamorphic basement, Neogene sediments, old volcanic tuffaceous formations, ignimbrites, old rhyolitic rocks, old dacitic and andesitic members, pyroclastic rocks, younger tuffs, lahar in different places, younger volcanics of acid composition and quaternary formations. Regarding its geological characteristics, the intensively eroded crystalline metamorphic basement appears in a very limited area (SE coastline). A not continuous series of Mio–Pliocenic marine sediments is lying above the crystalline basement; it begins with reddish conglomerates and ends up with well-bedded limestones, which at places turn to sandstones (Fytikas, 1977).

From Upper Pliocene Milos was affected by an extensive volcanism, which lasted until late Quaternary (Fytikas et al., 1986). The composition of Milos volcanic rocks shows a calcalkaline character ranging from andesites to rhyolites. The youngest Upper Pleistocene volcanic activity is concentrated in corre-

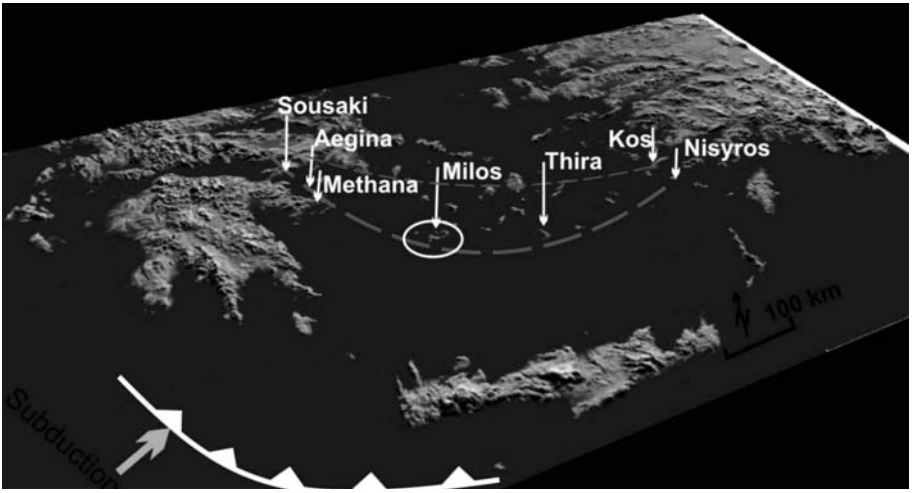

Fig. 1: Map of Greece showing Milos Island and the South Aegean Volcanic Arc.

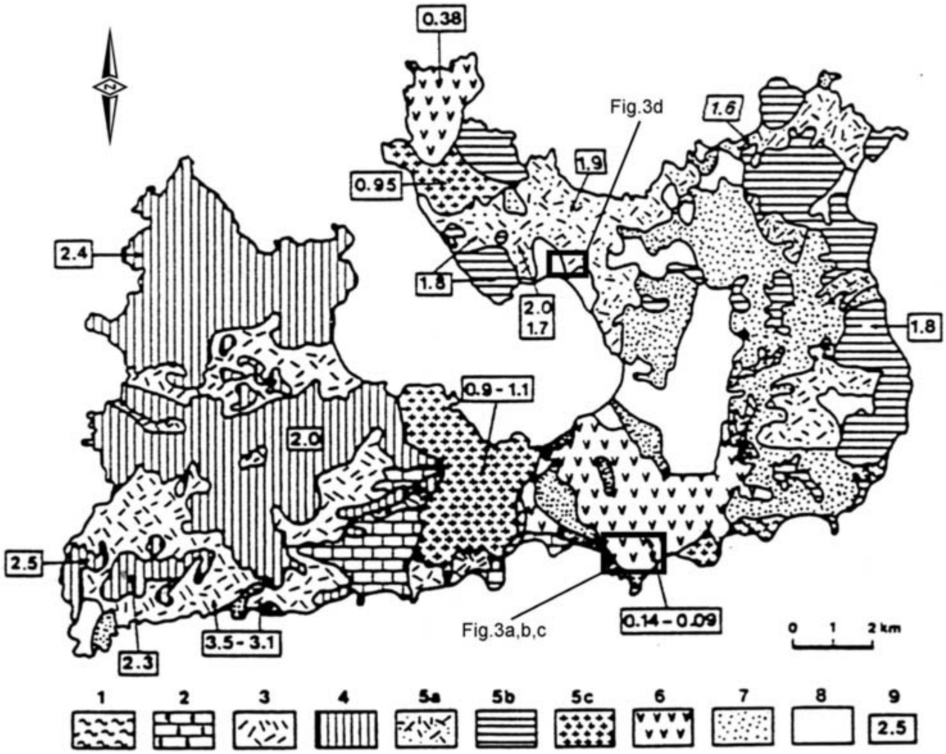

Fig. 2: Main geological units of Milos volcanic island (From Fytikas, 1976 modified). 1=Metamorphic basment; 2= Neogene sediments; 3= Basal pyroclastic series (Middle-Upper Pliocene); 4= complexes of domes and lava flows (Upper Pliocene); 5= Upper Pleistocene volcanics: pyroclastic series (5a), lava domes (5b) and Halepa and Plaka domes (5c); 6= Fyriplaka and Trachilas Rhyolitic complexes of Upper Pleistocene; 7= freatic activity products; 8= Quaternary sediments; 9= Radiometric ages from Angelier et al. (1977), Bigazzi and Radi (1981), Fytikas et al. (1976).

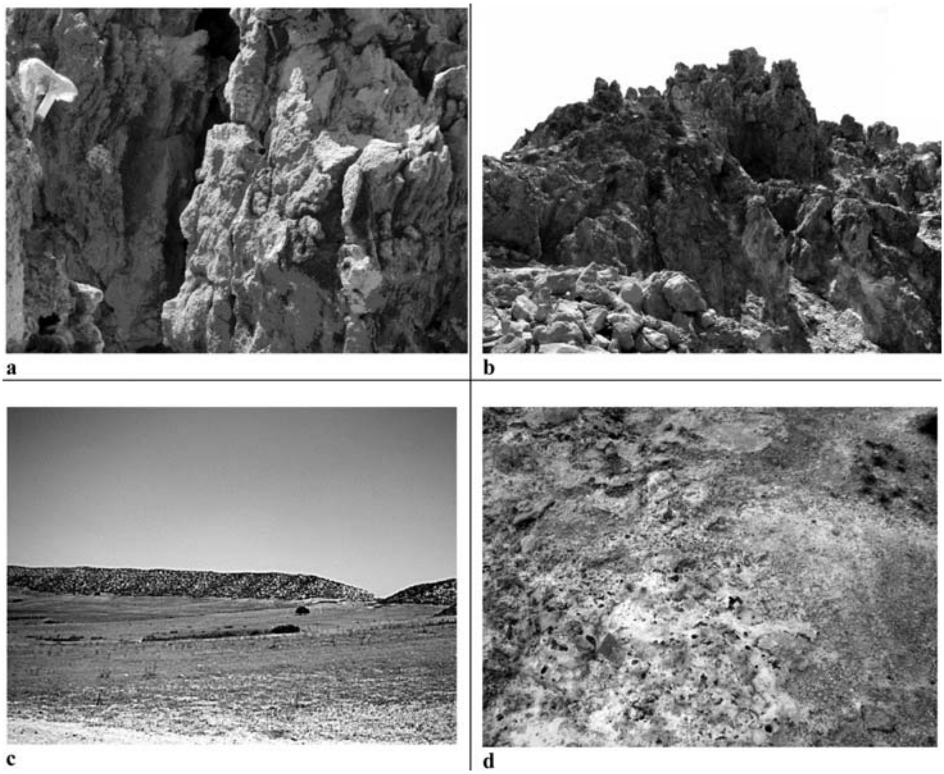

Fig. 3: a,b) Fumaroles at Kalamos degassing area, c) Crater of Fyriplaka volcano, d) Surface secondary minerals due to alteration phenomena of H_2S emanation, north of Adamas geothermal field. The locations of these photographs are noted on the map of Fig. 2.

spondence of the volcanic centres of Fyriplaka in the South and Trachilas in the North. In Trachilas the explosive activity began with the formation of a tuff ring mainly composed by pyroclastic surges; the surge deposits gradually pass to block and lapilli and finally to lava flows (Fytikas et al., 1986; Mitropoulos et al., 1987; Kelepertzis and Kyriakopoulos, 1991; Kyriakopoulos, 1998).

In the Fyriplaka area at least two tuff rings can be identified: a larger one (about 1500 m in internal diameter) and an inner and smaller one. The explosive activity leading to the formation of these tuff rings alternated with effusive episodes producing lava flows which ran to the NW and reached the sea inside the Gulf of Milos (Fytikas et al., 1986), Fig.2.

A decrease in the water content interacting with the magma is generally observed in the evolution of the eruptions: they usually start as phreatic and successively evolve into phreatomagmatic and magmatic activity; lava flows close the eruptive cycles (Fytikas et al., 1986).

3. Sampling and analytical methods

A total of 26 samples were collected from Kalamos and Adamas areas were intense gas emanation is occurring. The localities sites of the volcanic areas Kalamos and Fyriplaka in the south part and Adamas at the central part of the island are reported in Figure 3. Free gas samples were taken from natural gas manifestations like fumarolic discharges, soil gases, and mofettes and were collected at a depth of 50 cm through steel or nylon tubes connected to a syringe while bubbling gases were collected through inverted funnels. Samples were then stored into glass flasks equipped with vacuum stopcocks. Furthermore 78 samples of soil gases were analysed in the field for CO_2 concentration with a portable IR spectrometer.

Gas concentrations were measured at INGV in Palermo using the GC Perkin Elmer Clarus 500 equipped with Carboxen 1000 columns, HWD and FID detectors with methanizer. The gas samples were injected through an automated injection valve with a 1000 μL loop. Calibration was made with certified gas mixtures. Analytical precision (1σ) was always better than ±5%. The detection limits were about 1 ppm vol. for CO and CH_4, 2 ppm vol. for H_2, 6 ppm vol. for He, 20 ppm vol. for CO_2, 200 ppm vol. for O_2 and 500 ppm vol. for N_2. Analyses of carbon isotopes of CO_2 were carried out by using a Finnigan Delta plus mass spectrometer. Values are expressed in δ‰ vs. V-PDB, accuracy ±0.1 δ‰.

4. Health hazard from volcanic gases

Regarding health hazard related of volcanic gases at least 455 million people worldwide live within potential exposure range of a volcano that has been active in recent times. The effects of SO_2 on people and the environment vary widely depending on (1) the amount of gas a volcano emits into the atmosphere; (2) whether the gas is injected into the troposphere or stratosphere; and (3) the regional or global wind and weather pattern that disperses the gas.

The volcanic gases that pose the greatest potential hazard to people, animals, agriculture, and property are sulfur dioxide, carbon dioxide, and hydrogen fluoride. Locally, sulfur dioxide gas can lead to acid rain and air pollution downwind from a volcano.

Because carbon dioxide gas is heavier than air, the gas may flow into in low-lying areas and collect in the soil. The concentration of carbon dioxide gas in these areas can be lethal to people, animals and vegetation, Table 1.

Table 1. Physiologic effects of human exposure to H_2S (Beauchamp et al. 1984; WHO 2003).

Exposure ppm	Effect/observation
0.01–0.13	Odor threshold
0.3	Distinct odor
2	Bronchial constriction in asthmatic individuals
3.5	Increased eye complaints
5–10	Increased blood lactate concentration, decreased skeletal muscle citrate synthase activity, decreased oxygen uptake
3.5–20	Eye irritation
20	Fatigue, loss of appetite, headache, irritability, poor memory
50	Marked irritant action on conjunctiva and respiratory tract
100–200	Olfactory paralysis
250	Prolonged exposure causes pulmonary edema
500–1,000	Immediate death

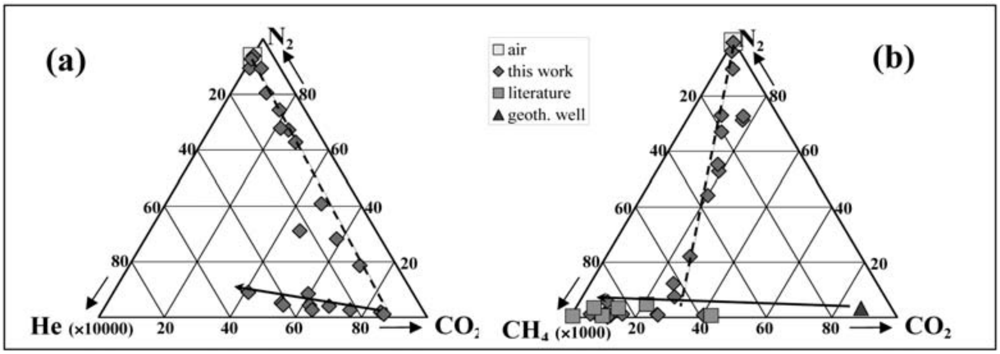

Fig. 4: – (a) He-N_2-CO_2 and (b) CH_4-N_2-CO_2 triangular plot of the gas samples collected at Milos. Dark gray squares and the geothermal well composition are from literature data. Dashed line shows the mixing between atmospheric air and geothermal gases. The arrows indicate CO_2 loss.

4.1 Hydrogen sulfide (H_2S)

Hydrogen sulfide (H_2S) is a colorless, flammable gas with a strong offensive odor. It is sometimes referred to as sewer gas. At low concentrations it can irritate the eyes and acts as a depressant; at high concentrations it can cause irritation of the upper respiratory tract and, during long exposure, pulmonary edema. A 30-minute exposure to 50 ppm results in headache, dizziness, excitement, staggering gait, and diarrhea, followed sometimes by bronchitis or bronchopneumonia, while concentrations above 500 ppm can be lethal within short time (Table 1). Continuous exposure to high concentration should be avoided. Moreover various studies (Loppi, 1996; Tretiach and Ganis, 1999) highlighted the adverse effects of volcanic/geothermal H_2S on nearby growing vegetation.

4.2 Carbon dioxide (CO_2)

Volcanoes release more than 130 million tonnes of CO_2 into the atmosphere every year. This colorless, odorless gas usually does not pose a direct hazard to life because it typically becomes diluted to low concentrations very quickly whether it is released continuously from the ground or during episodic eruptions. But in certain circumstances, CO_2 may become concentrated at levels lethal to people and animals. Carbon dioxide gas is heavier than air and the gas can flow into in low-lying areas; breathing air with more than 30% CO_2 can quickly induce unconsciousness and cause death.

5. Results and discussion

5.1 Geochemistry of the gases

Although Milos Island is not currently volcanically active, it is the site of intense old and recent hydrothermal processes. At the present time a high geothermal gradient (> 2,5 H.F.U.) occur. The high heat flow caused intense hydrothermal activity, which is responsible for many phreatic explosions. In some places the hydrothermal activity is expressed by the occurrence of many hot springs (30-85°C), fumaroles (98-102°C), hot grounds (100°C at a depth of 30-40cm) and submarine gas emissions, widespread on and around the island. Fyriplaka volcano is the expression of the most recent volcanic activity on the island and includes fumaroles, solfataras and hot grounds (Fytikas et al., 1986).

A preliminary survey of volcanic gas analyses shows that, with very few exceptions, the predominating constituents making up more than 95 % of the volcanic gas discharge are water vapor and

Table 2. Chemical composition of gas samples of Milos Island.

sample	type	date	He	H_2	O_2	N_2	CO	CH_4	CO_2	H_2S	$\delta^{13}C$	R/Ra	He/Ne
			ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	‰		
Milos C1 Fyriplaka	FG	1-06-2007	5	< 2	194900	789400	3.7	3.6	1200	100	n.d.	n.d.	n.d.
Milos C2 Fyriplaka	FG	1-06-2007	8	492	168500	725600	6.3	171	97200	200	n.d.	n.d.	n.d.
Milos C3 Fyriplaka	FG	1-06-2007	8	1873	145500	581400	11	471	263600	2000	-1.5	n.d.	n.d.
Milos C4 Fyriplaka	FG	1-06-2007	8	91	187500	771100	3.4	20	10600	100	n.d.	n.d.	n.d
Milos C5 Fyriplaka	FG	1-06-2007	5	29	182000	760900	4	46	40600	200	n.d.	n.d.	n.d.
Milos Fyriplaka	FG	20-06-2007	6	5	193800	777800	1	3.2	1500	n.d.	-0.1	n.d.	n.d.
Milos Adamas	SG	20-06-2007	12	596	101600	416000	3.9	986	482800	n.d.	0.3	n.d.	n.d.
Milos Paleochori 1	BG	21-06-2007	45	8	33300	119400	17	7533	838100	n.d.	n.d.	n.d.	n.d.
Milos Paleochori 2	BG	21-06-2007	69	< 2	19000	85700	14	10100	874400	n.d.	n.d.	n.d.	n.d.
Milos Paleochori 3	BG	21-06-2007	49	< 2	12000	62900	10	7929	901000	n.d.	-0.3	2.57	12.51
Milos Paleochori 4	BG	21-06-2007	37	< 2	13800	52700	8	6615	905300	n.d.	n.d.	2.52	20.23
Milos Fyriplaka	FG	12-10-2007	8	432	142600	627400	6	334	226000	n.d.	n.d.	n.d.	n.d.
Milos Mad 1	BG	12-10-2007	69	< 2	2800	73000	1	4877	896200	n.d.	-0.9	3.37	37.76
Milos Mad 2	SG	13-10-2007	7	237	166400	668500	5	109	160000	n.d.	1.6	n.d.	n.d.
Milos Paleochori	SG	22-10-2007	15	284	32800	315300	4	1593	650600	n.d.	-0.2	n.d.	n.d.
Milos M1	SG	21-03-2008	< 5	1304	170000	680100	1.6	206	129600	n.d.	n.d.	n.d.	n.d.
Milos M2	SG	21-03-2008	10	486	152600	635600	1.8	313	201500	n.d.	1.7	n.d.	n.d.
Milos M3	SG	21-03-2008	< 5	664	167300	672000	1	99	153300	n.d.	n.d.	n.d.	n.d.
Milos 1 Sinopi	BS	5-09-2008	50	< 2	9200	39100	1.5	2636	944100	n.d.	n.d.	2.97	12.64
Milos 2 Adamas DEH	BG	12-08-2008	15	13	425	20700	1.5	1405	966100	n.d.	-1.3	3.04	6.14
Milos 3 Paleochori	BS	12-08-2008	14	29	3800	12500	3.2	7448	957000	n.d.	-0.4	n.d.	n.d.
Milos 4 Adamas	SG	5-09-2008	12	1418	50300	199300	3	1717	750600	n.d.	-0.7	n.d.	n.d.
Milos 5 Paleochori	BS	4-09-2008	26	6660	91600	348900	14	5167	511800	n.d.	n.d.	n.d.	n.d.
Milos 6 Paleochori	BS	5-09-2008	80	149100	52100	143800	13	11000	657400	n.d.	n.d.	n.d.	n.d.
Milos DEH	BG	10-06-2009	28	< 2	4700	33400	1.6	2625	951200	n.d.	-0.4	n.d.	n.d.
Exploratory well (*)			n.d.	12000	11000	35000	n.d.	100	926000	15000	n.d.	n.d.	n.d.

Type: FG = fumarolic gas; SG = soil gas; BG = bubbling gas; BS = gas bubbling in sea.water – n.d. = not determined. (*) data from Minissale et al. (1997)

species containing carbon and sulfur in their various oxidation states such as CO_2, CO, SO_2, S_8 and H_2S together with H_2. In the case of Milos gases, water vapour is an important component only of the fumarolic gases. In the present study only the dry gas composition (i.e. excluding water vapour) has been determined and the analytical results are shown in table 2. Apart from atmospheric gases (O_2 and N_2) deriving from air contamination, the main gas is CO_2. The O_2, N_2 and CO_2 contents evidence a clear mixing trend between two end-member represented by the atmospheric air and a CO_2-dominated geothermal gas. Isotopic composition of the CO_2-carbon, displaying values close to 0‰ (range from –1.5 to 1.6 ‰), indicates that the main CO_2 source may be the reaction between the acidic hydrothermal solutions with underlying Neogene limestone deposits (Fytikas, 1989) as well as from thermal decomposition of subducted marine sediments. But a contribution from mantle CO_2 cannot be excluded. Such contribution is strongly suggested by the isotopic composition of the helium whose values (R/R_a ranging between 2.5 and 3.4) highlights a mantle component of at least 50% for this gas.

The He-N_2-CO_2 triangular plot (Fig. 4a) shows two alignments. The first belongs to the mixing trend between atmospheric air and the geothermal gas. The second pointing towards the He vertex is probably due to processes responsible of CO_2 loss like carbonate precipitation or CO_2 dissolution in water. The last process is mostly evident in those gases which where collected from manifestations bubbling in sea-water.

The gas composition of one exploratory well (Table 2) evidences the enrichment in H_2S of the geothermal fluids at Milos. But this gas is partially lost in the shallow environment due to dissolution in condensing water vapour and oxidation processes. Such processes producing H_2SO_4-rich condensates are responsible of the low pH values (2.9) measured in the fumarolic condensate at Aghia Kyriaki, on the south coast of Milos (Dominico and Papastamataki, 1975). The CH_4-N_2-CO_2 triangular plot (Fig. 4b) further evidences the processes that bring to CO_2 loss and the mixing processes between geothermal and atmospheric gases.

Carbon dioxide in the soils of Milos shows a wide range of concentrations from 0.01 to 99.8 % (table 3). Concentrations sustained by biologic activity within the soils are generally less than a few %, while higher concentrations are clearly due to uprising geothermal fluids. Notably the highest concentrations were found at Adamas and Kalamos areas close to the sites of the most recent volcanic activity (Fig. 5).

5.2 Gas hazard and environmental impact

Volcanic/geothermal areas release huge amounts of gases, which apart from having important influences on the global climate could have a strong impact both on the local environment and on human health. Gases have both acute and chronic effects. Carbon Dioxide and Sulphur gases are the main gases responsible for acute mortality due to their asphyxiating and/or toxic properties. The problem has long been neglected until the "Lake Nyos" catastrophe in 1986, in which about 1700 people were killed by a volcanic CO_2 emission, attracted the worldwide attention of the mass media.

Gas hazard is largely underestimated because it acts also during quiescent periods and also in areas were volcanic activity is nowadays extinct. Furthermore, although the frequency of occurrence is relatively high, the number of victims of each lethal accident is generally low and often the real cause of death is not properly recognized. As a consequence, the recently published database of volcanic disasters and incidents of the 20th century (Witham, 2005), which attributed the death of 2000 persons and the injury of nearly 3000 to volcanic gases, is probably largely incomplete. The most dangerous gas species is CO_2, responsible of more than 90% of the victims and of the worst episodes

Table 3. Soil CO_2 concentrations at -50 cm depth (in vol %) of Milos geothermal field.

ID	LAT	LONG	ALTITUDE	CO_2	ID	LAT	LONG	ALTITUDE	CO_2
1	36.668	24.493	146	7.93	41	36.677	24.485	68	0.50
2	36.669	24.493	146	6.99	42	36.695	24.545	55	0.05
3	36.668	24.493	133	2.30	43	36.695	24.544	17	0.05
4	36.668	24.493	145	3.77	45	36.694	24.544	17	0.21
5	36.668	24.493	146	12.80	46	36.694	24.538	95	0.22
6	36.667	24.493	138	11.17	47	36.675	24.513	27	7.58
7	36.667	24.492	145	4.90	48	36.675	24.515	30	0.22
8	36.667	24.492	140	7.90	49	36.675	24.513	27	1.30
9	36.667	24.492	140	6.90	50	36.675	24.513	27	20.20
10	36.666	24.492	140	0.09	51	36.731	24.448	10	22.07
11	36.666	24.493	140	6.42	64	36.731	24.448	10	54.60
12	36.666	24.493	148	0.18	65	36.731	24.448	10	77.08
13	36.665	24.493	144	0.09	66	36.731	24.448	10	95.70
14	36.665	24.493	144	0.78	67	36.731	24.448	10	48.70
15	36.665	24.493	144	0.14	68	36.731	24.448	10	99.80
16	36.666	24.494	144	0.22	69	36.731	24.449	10	79.80
17	36.666	24.494	106	0.14	70	36.731	24.449	10	55.70
18	36.667	24.494	106	0.19	71	36.731	24.449	15	2.20
19	36.667	24.494	106	0.54	72	36.731	24.449	8	1.30
20	36.667	24.493	138	1.29	73	36.731	24.450	8	0.99
22	36.667	24.493	138	1.78	74	36.731	24.450	11	0.90
23	36.667	24.493	138	2.70	75	36.731	24.448	6	18.00
24	36.667	24.493	136	0.46	76	36.731	24.448	6	18.00
25	36.666	24.493	144	0.27	77	36.731	24.449	6	2.80
26	36.666	24.492	131	0.06	78	36.730	24.449	5	1.15
27	36.666	24.491	114	7.71	79	36.731	24.448	6	60.00
28	36.665	24.491	133	18.20	80	36.731	24.448	9	20.00
29	36.665	24.491	110	2.10	81	36.732	24.448	9	5.10
30	36.665	24.491	110	1.70	82	36.732	24.447	11	3.00
31	36.666	24.491	114	0.70	83	36.732	24.446	13	0.25
32	36.666	24.491	114	1.22	84	36.732	24.445	30	0.20
33	36.667	24.491	124	1.14	85	36.732	24.448	21	0.10
34	36.669	24.492	128	1.30	86	36.733	24.448	32	0.10
35	36.670	24.492	91	5.07	87	36.734	24.448	44	0.10
36	36.670	24.492	109	2.62	8	36.735	24.447	51	0.10
37	36.670	24.491	109	1.42	89	36.736	24.446	58	0.10
38	36.668	24.491	130	0.50	90	36.737	24.445	69	0.15
39	36.671	24.490	112	0.22	91	36.731	24.450	11	0.10
40	36.674	24.487	77	0.01	92	36.731	24.451	25	0.10

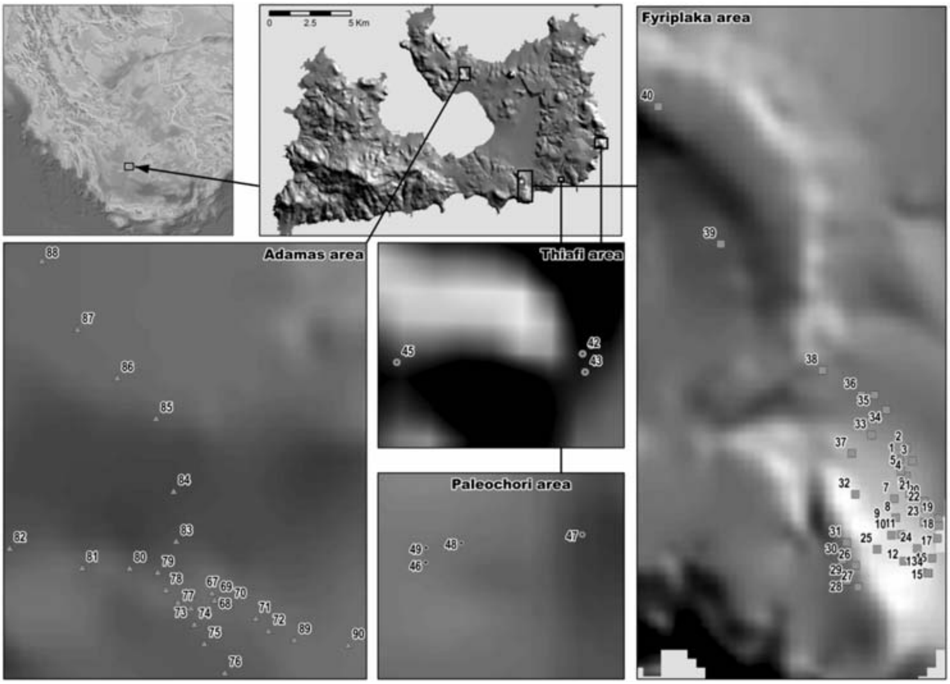

Fig. 5: Distribution of the soil gas sampling points of the four sampling areas on a shaded relief map.

(Lake Nyos and Lake Monoun, Cameroon and Dieng Plateau, Indonesia), but lethal episodes are also attributed to sulphur gases (SO_2 and H_2S).

Being heavier than air, CO_2 and H_2S can accumulate in topographic depressions and enclosures, and in areas with high fluxes their concentrations can exceed 10% and 100 ppm, respectively, which can be lethal to both animals and humans. At Milos Island hazardous concentrations of CO_2 (more than 90 %) and H_2S (up to 2000 ppm) are measured near the main emanation Kalamos and Fyriplaka areas.

People living in anomalous degassing areas are generally aware of the danger posed by gas accumulation, but nevertheless volcanic gases cause many fatalities each year worldwide (Witham, 2005). Even though the gas hazard at Milos appears restricted to limited areas, it should not be neglected, especially its effects on the most exposed people: children, workers involved in excavation activities and tourists who use public baths.

The H_2S dispersing in the surrounding atmosphere displays concentrations of some ppm that produces surely annoying smell and represents also a potential chronic health impact for the nearby living persons. Furthermore oxidizing reactions in the atmosphere transforms H_2S in SO_2, locally increasing the acid burden through wet and dry deposition. Such processes are more intense during the summer season when high temperature and strong incoming solar radiation increases the formation of strong oxidant species like OH and O_3.

Furthermore, where gas emanations are very high, the soils are altered and covered with thin layers of secondary minerals as alunite, magnesite and sulphur. In these areas, the extreme acidity of the fumarolic condensates, which is responsible of the high mobility of harmful elements during alteration processes, could negatively impact biota of the surrounding terrestrial and marine environments. Although such impact at Milos has not been studied yet, it is worth noting that vegetation around the hydrothermal manifestations is very stunted probably due to the bioaccumulation of the mobilized toxic elements.

6. Conclusions

The main gas manifestations at Milos show a typical hydrothermal composition. Excluding water vapour, the main gas species is represented by carbon dioxide. Its carbon isotopic composition points to a main origin from carbonate rocks although a significant mantle contribution cannot be ruled out. Other typical hydrothermal gases like hydrogen, methane and hydrogen sulphide display sometimes concentrations up to a few percent.

Soil gases show characteristic mixing trend between atmospheric air and deep geothermal gases. The latter implies their highest contents close to the fumarolic areas of Adamas and Kalamos. These areas show very high risk of gas hazard, and gas emissions could have a strong impact on the local environment.

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8. References

Angelier, J., Cantagrel, M., Vilminot, C., 1977. Neotectonique cassante et volcanisme plioquaternaire dans l'arc eggeen interne: I'lle de Milos (Grece). *Bull. Soc. Geol. France,* 19, 119-121.

Beauchamp, R.O., Jr, Bus, J.S., Popp, J.A., Boreiko, C.J., Andjelkovich, D.A., 1984. A critical review of the literature on hydrogen sulfide toxicity. *Crit Rev Toxicol* 13:25–97.

Chiodini, G., Cioni, R., Leonis, C., Marini, L., Raco, B., 1993. Reactions governing the chemistry of crater fumaroles from vulcano island Italy, and implications for volcanic surveillance. *Appl. Geochem*., 8, 357-371.

Delmelle, P. and Stix, J., 2000. Volcanic Gases. In: *Encyclopedia of Volcanoes* (eds. H. Sigurdsson B. Houghton S. McNutt H. Rymer J. Stix), Academic Press, San Diego, 803-815.

Dewey, J.F. and Sengor, A.M.C., 1979. Aegean and surrounding regions: complex multiplate and continuum tectonicsin convergent zone. *Bull. Geol. Soc. Am*. 90, 84-92.

Dominco, P. and Papastamataki, A. 1975. Characteristics on Greek geothermal waters. 2nd U.N. Symp. Dev. Use Geoth. Resources. S. Francisco.

Fytikas, M. Giuliani, O. Innocenti, F. Marinelli, G., Mazzuoli, R., 1976. Geochronological data on recent magmatism of the Aegean Sea. *Tectonophysics,* 31, T29-T34.

Fytikas, M., Innocenti, F., Kolios, N., Manetti, P., Mazzuoli, R., Poli, G., Rita, F., Villari, L., 1986. Volcanology and petrology of volcanic products from the island of Milos and neighbouring islets. *J. Volcanol.Geotherm. Res*. 28, 297-317.

Fytikas, M., 1989. Updating of the geological and geothermal research on Milos Island. *Geothermics,* 18, 485-496.

Giggenbach, W.F., 1996. Chemical composition of volcanic gases. In: *Monitoring and Mitigation of Volcano Hazards* (R. Scarpa, R.I. Tilling, editors) Springer, Berlin, pp. 221-256.

Kelepertzis, A. and Kyriakopoulos, K., 1991. Mineralogy and geochemistry of the Mn-mineralization from Vani area of Milos island-its genesis problem. Prakt. Acad. of Athens, vol. 66, pp. 107-121.

Kyriakopoulos, K., 1998. K-Ar and Rb-Sr isotopic data of white micas from Milos island geothermal boreholes field. *Annal. Geol. Pays Hell.* 38, p. 37-48.

Loppi, S., 1996. Lichens as bioindicators of geothermal air pollution in Central Italy. *Bryologist* 99, 41–48.

Marty, B. and Jambon, A., 1987. $C/^3He$ in volatile fluxes from the solid earth: implications for carbon geodynamics *Earth Planet. Sci. Lett,* 83,16-26.

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

Mitropoulos, P., Tarney, J., Saunders, D., Marsh, N., 1987. Petrogenesis of cenozoic volcanic rocks from the Aegean Island Arc. *J. Volcanol.Geotherm. Res*, 32, 177-193.

McKenzie, D., 1972. Active tectonics of the Mediterranean region. *Geoph. J. R. Astr. Soc.*, 30, 55-71.

Mörner, N.A., Etiope, G., 2002. Carbon degassing from the lithosphere, *Global Planet. Change 33*, 185-203.

Papadopoulos, B.A., Kondopoulou, D.P., Leventakis, G.A., Pavlides, S.B., 1986. Seismotectonics of the Aegean Region. *Tectonophysics,* 124, pp. 67-84.

Papazachos, B.C., 1990. Seismisity of the Aegean and surrounding area. *Tectonophysics*, 178, 287-308.

Spakman, W., Wortel, M.J.R., Vlaar, N.J., 1988. The Hellenic subduction zone: a tomographic image and its geodynamic implications. *Geophys. Res. Lett.* 15, 60-63.

Tretiach, M., Ganis, P., 1999. Hydrogen sulphide and epiphytic lichen vegetation: a case study on Mt. Amiata (Central Italy). *Lichenologist* 31, 163–181.

Truffert, C., Chamot-Rooke, N., Lallemant, S., De Voogd, B., Huchon, P., Le Pichon, X., 1992. A crustal-scale cross section of the western Mediterranean ridge from deep seismic data and gravity modelling. *Geophys. J. Int.* 114, 360-372.

Witham, C.S., 2005. Volcanic disasters and incidents: A new database. *J. Volcanol. Geotherm. Res.*, 148, 191–233.

WHO, 2003. *Hydrogen sulphide: human health aspects*. Concise International Chemical Assessment Document 53, World Health Organization, Geneva, pp 26.