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GEOCHEMICAL CHARACTERIZATION OF NATURAL GAS MANIFESTATIONS IN GREECE

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Abstract

The Greek region is characterized by intense geodynamic activity with widespread volcanic, geothermal and seismic activity. Its complex geology is reflected in the large variety of chemical and isotopic composition of its gas manifestations.

Basing on their chemical composition the gases can be subdivided in three groups, respectively CO_2, CH_4 or N_2-dominated. On oxygen-free basis these three gases make up more than 97% of the total composition. The only exceptions are fumarolic gases of Nisyros that contain substantial amounts of H_2S (up to more than 20%) and one sample of Milos that contains 15% of H_2. CO_2-dominated gases with clear mantle contribution in their He isotopic composition (R/R_a corrected for air contamination ranging from 0.5 to 5.7) are found along the subduction-related south Aegean active volcanic arc and on the Greek mainland close to recent (upper Miocene to Pleistocene) volcanic centers. These areas are generally characterized by active or recent extensive tectonic activity and high geothermal gradients. On the contrary, gases sampled in the more external nappes of the Hellenide orogen have generally a CH_4- or N_2-rich compositions and helium isotope composition with a dominant crustal contribution (R/R_a corr < 0.2).

The chemical and isotopic characteristics of the emitted gas display therefore a clear relationship with the different geodynamic sectors of the region. Gas geochemistry of the area contributes to a better definition of the crust-mantle setting of the Hellenic region.

Key words: *natural gas manifestations, gas chemistry, He- and C- isotope composition.*

1. Introduction

The Hellenic territory has a very complex geodynamic setting deriving from a long and complicated geological history. Many of the geologic features of Greece are still argument of strong debate and Zeilinga de Boer (1989) defined its geodynamic situation as "The Greek enigma". The Hellenic territory is also the site of intense seismic activity (Burton et al., 2004) and enhanced geothermal gradient (Fytikas and Kolios, 1979). This together with the presence of an active volcanic arc favours the existence of many cold and thermal gas manifestations.

Until now only scarce data on chemical and isotopic composition of these gas manifestations have been published. Furthermore these data are either limited to single volcanic/geothermal systems

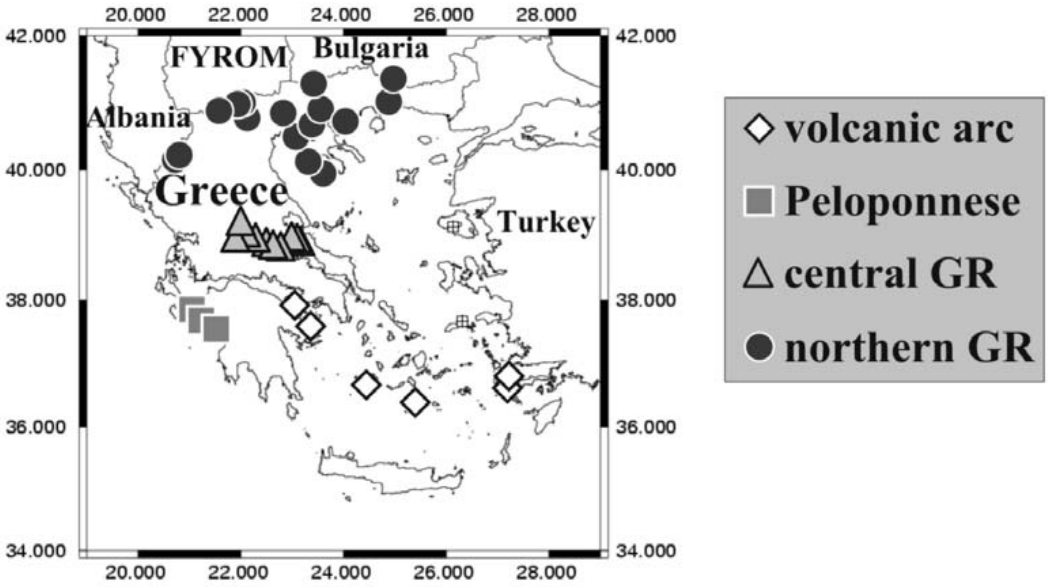

Fig. 1: Geographic distribution of the sampled gas manifestations.

(Marini and Fiebig, 2005; D'Alessandro et al., 2008) or if considering geographically wider areas they refer only to their chemical (Minissale et al., 1989; 1997) or to their noble gas isotopic (Shimizu et al., 2005) composition. In the present study both the chemical and the isotopic composition (C, He) of 52 samples collected along the whole Hellenic territory has been analysed in an attempt to reveal possible relationships with the geodynamic situation.

2. Study area and methods

2.1 Geological setting

The Aegean region is a concentrate of the main geodynamic processes that shaped the Mediterranean region: oceanic and continental subduction, mountain building, high-pressure and low-temperature metamorphism, backarc extension, post-orogenic collapse, metamorphic core complexes, gneiss domes are the ingredients of a complex evolution that started at the end of the Cretaceous with the closure of the Tethyan ocean along the Vardar suture zone (Jolivet and Brun, 2008).

The Greek and west Anatolian region was affected by a Tertiary and Quaternary volcanism with an orogenic signature. The oldest products are of upper Eocene-Oligocene age and are exposed in limited volumes in the northern part of Greece. The volcanic activity reached a climax in the Lower Miocene and was exhausted by the Middle Miocene (Yilmaz et al., 2001).

The Paleogene Hellenide orogeny of Greece and its eastward continuation into western Turkey resulted from collision of the Apulian microcontinental fragment in the Eocene to Oligocene with the Pelagonian, Rhodope, and Serbo-Macedonian fragments, which had previously accreted to the southern margin of Eurasia in the Cretaceous. Subsequent extension in the Aegean was rapid, likely due

to subduction rollback over residual oceanic crust of the African plate, whereas Anatolia had been bounded by African continental crust south of Cyprus since the Early Miocene. This regional extension and the thermal effects of asthenospheric upwelling, related to changes in the geometry of subducting slabs, have been interpreted as causing magma genesis principally within the lithospheric mantle (Pe-Piper and Piper, 2002).

At the south Aegean Volcanic Arc the volcanic activity started during the Upper Pliocene (Fytikas et al., 1986) and is still active today mainly in the form of solfatara activity. The calc-alkaline volcanic activity of Southern Aegean region developed in various volcanic centers from Sousaki to Nisyros through Methana-Poros, Milos and Santorini. The volcanic products are dominated by lava domes and lava flows with associated minor pyroclastic breccias and felsic ignibritic covers (Mitropoulos et al., 1987). The final activity of this orogenic cycle is characterized by the presence of K-rich shoshonites and latites with ultrapotassic character.

2.2 Sampling and analytical methods

A total of 52 samples were collected along the whole Hellenic territory (Fig. 1). Free gas samples were taken from natural gas manifestations like fumarolic discharges, soil gases, mofettes, gas bubbling in cold or thermal waters and also from wells drilled either for groundwater or carbon dioxide abstraction or for geothermal exploration. Water for dissolved gas analyses were collected in glass vials sealed underwater.

Fumarolic gas discharges and soil gases 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.

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 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. He concentrations less than 6 ppm were determined during He isotopic analysis with a detection limit of about 0.1 ppm. Dissolved gases in water samples were extracted using the head-space equilibration method according to Capasso and Inguaggiato (1998).

Analyses of carbon isotopes of CO_2 were carried out by using a Finnigan Delta plus mass spectrometer. Values of carbon isotope of CO_2 are expressed in δ‰ vs. V-PBD, accuracy being 0.1 δ‰. The method proposed by Capasso et al. (2005) was used for determination of the $\delta^{13}C$ of total dissolved inorganic carbon (TDIC). The theoretical equilibrium composition of a free CO_2 gas phase was calculated considering the fraction of all dissolved carbon species (H_2CO_3, HCO_3^- and CO_3^{2-}) and the relative fractionation factors.

The He-isotope ratio in the gas samples was analysed directly from the sample bottles after purification in the high-vacuum inlet line of the mass spectrometer. The isotope composition of dissolved He was analysed by headspace equilibration, following the method proposed by Inguaggiato and Rizzo (2004). He isotopes were measured with a modified double-collector mass spectrometer (VG 5400-TFT). $^3He/^4He$ ratios, determined against an air standard, are referred here to the atmospheric ratio ($R_a = 1.386 \times 10^{-6}$) as R/R_a. Measured values were corrected for the atmospheric contamination of the sample on the basis of its $^4He/^{20}Ne$ ratio (Sano and Wakita, 1985) determined with a quadrupole mass spectrometer (QMS, VG Quartz).

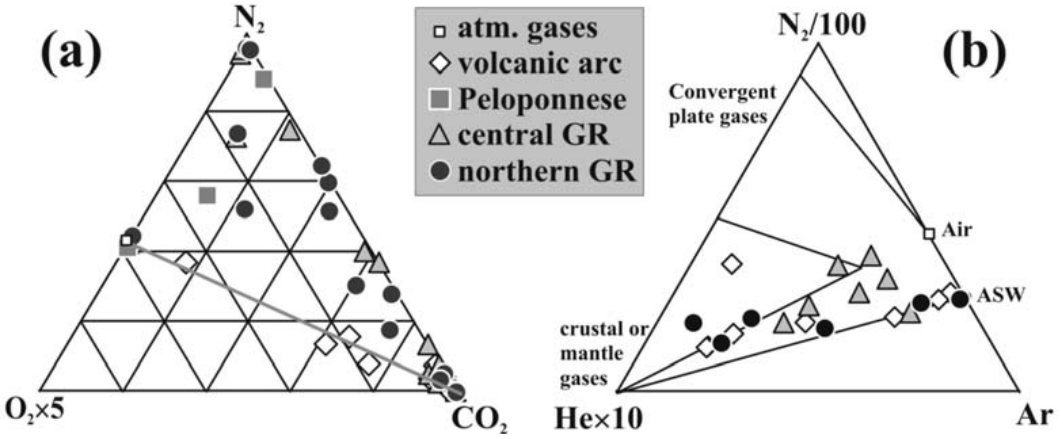

Fig. 2: a) O_2-N_2-CO_2 triangular plot and b) He-N_2-Ar triangular plot. Symbols as in Fig. 1 refer to the geographical distribution of the sampling sites.

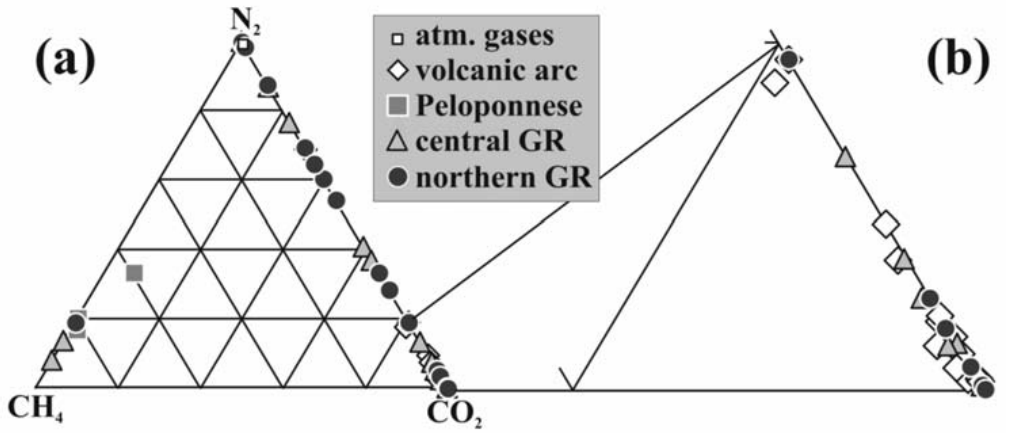

Fig. 3: a) CH_4-N_2-CO_2 triangular plot. b) enlargement of the CO_2 vertex. Symbols as in Fig. 1 refer to the geographical distribution of the sampling sites.

3. Results and discussion

3.1 Chemical composition of the gases

The results of the chemical analyses are listed in Table 1. They are reported as dry gases excluding water vapour, which is significant only in the fumarolic gas samples of Nisyros. The gas samples display a very large variability in chemical composition. Helium ranges from 0.4 up to 2940 ppm and shows a fair positive correlation with N_2. Only 21 samples have detectable H_2 (> 2 ppm) concentrations ranging from 5 up to 149000 ppm. Oxygen concentrations range from below the detection limit (< 200 ppm – 11 samples) up to 193000 ppm. The concentrations of N_2, CH_4 and CO_2 range from 600 to 978000, from less than 1 to 915000 and from 27 to 993000 ppm respectively. The last three species represent always the main gas component and all the samples can be subdivided in N_2^-, CH_4^- and CO_2^- dominated gases. On oxygen-free basis these three gases represent generally more than 97% of the total composition. The only exceptions are fumarolic gases of Nisyros that contain substantial amounts

Table 1. Chemical and isotopic composition of gas samples.

sample	lat	long	date	He	H_2	O_2	N_2	CH_4	CO_2	$\delta^{13}C(CO_2)$	R/Ra	He/Ne	R/Ra c	±1σ
			dd-mm-yy	ppm	ppm	ppm	ppm	ppm	ppm	‰ vsPDB				
Nisyros (PP9S)	36.583	27.166	10-10-07	30	16000	1600	8100	1760	743000 -	0.6	5.69	22	5.76	0.048
Nisyros (AM) 36.582	27.164	11-10-	07	33	9230	500	6200	805	809000	-0.4	5.78	40	5.82	0.063
Nisyros (S4)	36.578	27.169	12-10-07	27	6200	1100	4900	4400	792000	-0.9	5.72	12	5.86	0.048
Thermia (Kos)	36.814	27.192	25-07-08	43	< 2	38400	89600	427	847000	n.d.	n.d.	n.d.	n.a.	n.a.
Palea Kameni	36.399	25.380	07-05-96	1.1	3580	750	6400	4	980000	-1.1	3.34	4	3.52	0.053
Santorini Kameni B	36.404	25.396	06-10-07	7	11700	40800	178000	119	759000	0.5	3.35	2	3.81	0.023
Milos Mad 1	36.694	24.482	12-10-07	69	< 2	2800	73000	4880	896000	-0.9	3.37	38	3.39	0.034
Milos C3 (Fyriplaka)	36.668	24.492	01-06-07	8	1870	145000	581000	471	264000	-1.5	n.d.	n.d.	n.a.	n.a.
Milos 1 (Sinopi)	36.727	24.428	05-09-08	50	< 2	9200	39100	2640	944000	n.d.	2.97	13	3.02	0.004
Milos 2 (Adamas)	36.725	24.451	12-08-08	15	13	425	20700	1400	966000	-1.3	3.04	6	3.15	0.004
Milos 3 (Paleochori)	36.670	24.501	12-08-08	14	29	3800	12500	7450	957000	-0.4	n.d.	n.d.	n.a.	n.a.
Milos 6 (Paleochori)	36.668	24.501	05-09-08	80	149000	52100	144000	11000	657000	-0.7	n.d.	n.d.	n.a.	n.a.
Methana (MET 46)*	37.598	23.406	11-06-06	0.5	106	< 200	4900	42	966000	-1.0	2.34	3	2.48	0.034
Methana (Pausanias)*	37.638	23.360	23-06-06	0.5	< 2	5600	30900	17	970000	-2.0	2.06	2	2.22	0.063
Methana (Thiafy) *	37.597	23.405	24-06-06	20	29	6700	42200	717	942000	-1.4	2.55	22	2.57	0.022
Sousaki well	37.933	23.087	03-06-06	1.3	22	270	4900	61	987000	-1.5	0.64	7	0.62	0.013
Sousaki cave	37.935	23.087	03-06-06	37	< 2	1000	25700	10800	966000	-1.7	0.20	120	0.19	0.005
Loutra Killini	37.857	21.111	28-05-07	212	19	600	167000	803000	17100	-15.4	0.05	12	0.03	0.002
Katakolo mare	37.645	21.319	28-05-07	454	< 2	53600	190000	741000	2300	n.d.	0.08	119	0.08	0.007
Katakolo volcano 3	37.642	21.316	28-05-07	247	466	35900	317000	563000	69100	-5.1	0.04	43	0.04	0.001
Termopotamos	38.858	23.049	09-11-05	0.4	< 2	6200	26500	298	949000	-2.9	0.87	2	0.85	0.045
Ipatis	38.897	22.277	14-09-06	74	5	8400	52400	4600	929000	-5.2	n.d.	n.d.	n.a.	n.a.
Ipatis 2	38.894	22.281	14-09-06	139	< 2	< 200	25400	5400	958000	n.d.	0.06	974	0.06	0.001
Kammena Vourla	38.774	22.776	27-03-08	861	< 2	5100	762000	1783	232000	-9.4	0.48	222	0.48	0.010
Psoroneria 1	38.803	22.497	27-03-08	827	< 2	4000	407000	612	588000	-6.0	0.07	455	0.07	0.003
Psoroneria 2	38.804	22.495	27-03-08	890	< 2	< 200	367000	643	624000	-5.3	0.08	660	0.08	0.003
Amplas	38.922	22.052	28-03-08	57	24	600	81600	915000	100	n.d.	0.05	56	0.04	0.001
Archani #	38.983	22.162	28-03-08	25	< 2	5540	961000	33900	27	n.d.	n.d.	n.d.	n.a.	n.a.

Table 1. Continued

sample	lat	long	date	He	H_2	O_2	N_2	CH_4	CO_2	$\delta^{13}C(CO_2)$	R/Ra	He/Ne	R/Ra c	±1σ
			dd-mm-yy	ppm	ppm	ppm	ppm	ppm	ppm	‰ vsPDB				
Platystomo #	38.972	22.097	26-06-09	103	34	425	853000	135000	1100	-24.3(°)	0.10	15.7	0.09	0.002
Gialtra	38.850	22.987	29-03-08	397	< 2	39000	864000	954	130000	-10.7	0.44	81	0.44	0.014
Edipsos 2	38.855	23.049	29-03-08	1.8	< 2	< 200	2600	861	991000	-3.0	0.42	55	0.42	0.005
Ilion	38.852	23.128	29-03-08	102	< 2	800	75500	1632	919000	-2.6	0.25	341	0.25	0.006
Termopiles	38.793	22.528	28-03-08	213	< 2	< 200	133000	745	855000	-5.8	0.17	544	0.17	0.010
Smokovo	39.130	22.012	11-10-08	103	28	< 200	136000	850000	100	n.d.	0.05	55	0.04	0.007
Termopigi	41.281	23.363	05-10-04	33	< 2	800	13600	622	978000	-2.1	0.60	110	0.60	0.004
Pozar	40.971	21.914	27-05-08	475	< 2	61700	652000	1	289000	-5.1	0.72	68	0.72	0.006
Promachoi	40.991	21.980	27-05-08	259	< 2	34700	820000	< 1	118000	-7.4	1.27	30	1.27	0.012
Ninfopetra	40.689	23.355	30-05-08	2540	15	2700	968000	1680	5400	n.d.	0.05	304	0.05	0.000
Eleftere	40.736	24.091	30-05-08	27	< 2	800	51700	526	919000	-0.8	0.48	19	0.47	0.004
Nigrita	40.898	23.554	30-05-08	1.2	< 2	< 200	1300	26	988000	-1.7	0.33	20	0.32	0.003
Sani	40.102	23.313	31-05-08	597	8	< 200	192000	814000	3300	n.d.	0.63	2823	0.63	0.005
Amarantos	40.175	20.731	02-06-08	7	< 2	192700	777000	10	1200	n.d.	n.d.	n.d.	n.a.	n.a.
Pikrolimni #	40.830	22.827	29-05-08	313	< 2	19300	328000	22	653000	-6.4(°)	0.33	5	0.31	0.005
Souroti #	40.467	23.086	30-05-08	45	< 2	3390	283000	951	712000	-3.0(°)	0.35	5	0.33	0.009
Doumbia #	40.530	23.320	30-05-08	537	< 2	9890	536000	789	453000	-5.1(°)	0.40	12	0.39	0.014
A. Paraskevi #	39.924	23.590	31-05-08	6	22	1780	601000	915	396000	-1.4(°)	n.d.	n.d.	n.a.	n.a.
Kabasilos #	40.106	20.708	02-06-08	1320	< 2	1420	978000	2320	16700	-10.3(°)	0.14	307	0.14	0.005
XNT-1 (Thermes)	41.348	25.012	26-08-08	2940	< 2	< 200	631000	1010	346000	-2.5	0.43	218	0.43	0.004
Marina 2	40.861	21.491	04-03-07	25	< 2	4600	35400	1660	950000	-0.3	0.24	31	0.24	0.003
Mesochori 2	40.872	21.528	01-06-08	1.7	60	< 200	3100	353	992000	-1.5	0.66	6	0.64	0.005
Kampos	40.903	21.488	01-06-08	0.4	< 2	< 200	600	22	993000	-1.7	0.46	3	0.40	0.003
Ikaria (Ag. Kyr.1)	37.628	26.308	01-10-06	58	< 2	86600	860000	< 1	35900	-19.6	n.d.	n.d.	n.a.	n.a.

R/R_a is the Helium isotopic ratio normalised to the atmospheric ratio while R/Ra c is the same ratio corrected for air contamination considering the measured He/Ne values. ± 1σ error of the R/Ra c value. * Analyses previously published in D' Alessandro et al, 2008. # Dissolved gas sample. °Theoretical equilibrium values of CO_2 calculated from the measured total dissolved inorganic carbon. n.d. not determined, n.a. not applicable.

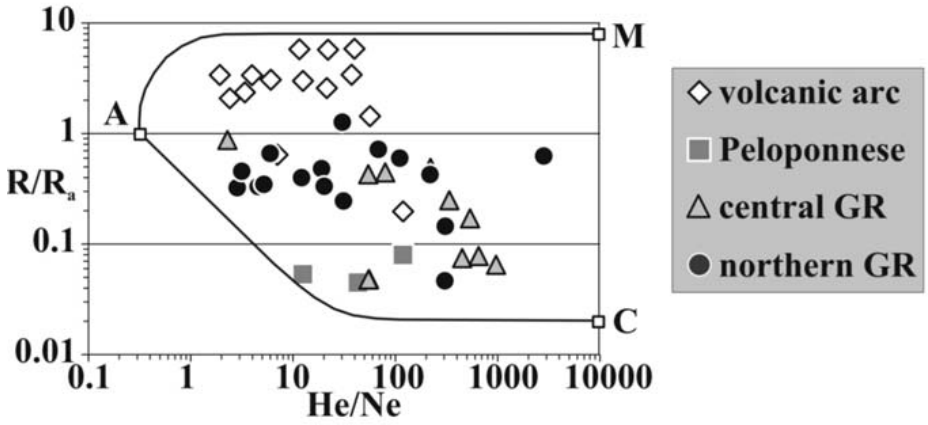

Fig. 4: R/R_a vs. He/Ne plot of the natural gas manifestations of Greece. A, M and C represent three possible end-members: atmospheric air, MORB-like mantle and crust. The mixing lines between A and M and between A and C are also plotted.

of H_2S (up to more than 20%) and one sample of Milos that contains 15% of H_2.

The O_2-N_2-CO_2 triangular plot (Fig. 2a) reveals that only few samples plot close to the point representing atmospheric air excluding important contaminations for most samples. Furthermore most samples display N_2/O_2 ratios much higher than the atmospheric one indicating that the atmospheric component deriving from meteoric recharge has probably been modified by redox reactions in the subsoil. Great contributions of N_2 deriving from slab-sediments can be ruled out by the N_2/Ar ratios, which are generally close to the atmospheric, or the air-saturated water ratios (Fig. 2b). Furthermore most of the samples show a strong contribution of helium deriving either from a crustal or a mantle source.

The CH_4-N_2-CO_2 triangular plot (Fig. 3a) shows that only 6 samples display a CH_4-dominated composition comprising all 3 samples collected in the Peloponnese, two samples of central Greece and one of northern Greece. N_2- and CO_2-dominated gases display on the same plot a mixing line (Fig. 3a). To the latter group, the most abundant (32 samples), belong all the samples collected along the active south Aegean volcanic arc (Fig. 3b) except one sample of Milos (Fyriplaka) contaminated with atmospheric air (Fig. 2a). Most of the N_2-dominated gases were collected in northern Greece (Fig. 3a).

3.2 Isotopic composition of the gases

The results of the isotopic analyses are listed in table 1. He isotopic values, expressed as $^3He/^4He$ ratio normalised to the atmospheric one ($R_a = 1.386 \times 10^{-6}$), range from 0.03 to 5.78 R/R_a. Measured values corrected for the atmospheric contamination of the sample on the basis of its $^4He/^{20}Ne$ ratio (Sano and Wakita, 1985) display a similar range (R/R_a corr 0.03 – 5.86). Such a wide range is indicative of different sources for the helium in the studied gases.

In Figure 4 the measured R/R_a values are plotted against the $^4He/^{20}Ne$ ratio together with the characteristic composition of three possible sources, the atmosphere (A), a MORB-like mantle (M) and the crust (C). The plot excludes strong atmospheric contaminations because only few samples display low $^4He/^{20}Ne$ ratios close to the characteristic end-member of atmospheric air. Samples col-

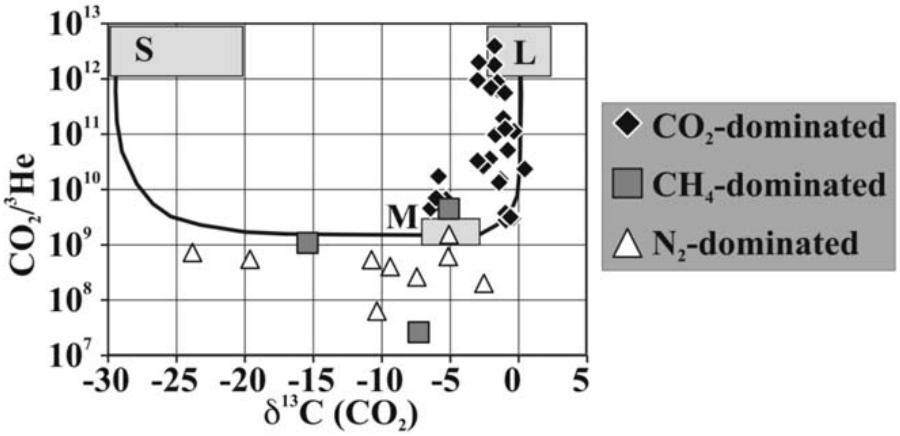

Fig. 5: $CO_2/^3He$ vs. $\delta^{13}C(CO_2)$ plot of the natural gas manifestations of Greece. The endmember compositions for sediments (S), MORB-like mantle (M) and limestones (L) are $\delta^{13}C(CO_2)$ = –30‰, –5‰ and 0‰; and $CO_2/^3He$ = 1´10^{13}, 2´10^9 and 1´10^{13}, respectively (Sano and Marty, 1995).

lected along the volcanic arc display the highest mantle contribution with all but the samples collected at Sousaki having values above 1 R/R_a. A few samples, among which are all those collected in the Peloponnese, display a prevailing crustal imprint ($R/R_a < 0.2$). Most of the samples display intermediate helium isotopic composition (R/R_a between 0.2 and 1) evidencing contributions of both deep sources (mantle and crust).

The carbon isotopic composition of CO_2 in the free gas samples ranges from –19.6 to +0.5 $\delta^{13}C$ ‰ (vs. V-PDB). For the dissolved gas samples the theoretical isotopic composition of gaseous CO_2 in equilibrium with the liquid phase has been calculated from the following measured parameters, temperature, $\delta^{13}C$ of the total dissolved inorganic carbon, dissolved CO_2 concentration and alkalinity, considering all fractionation factors between gas and all dissolved carbon species (Zhang et al., 1995). The obtained values range from –24.3 to –1.4 $\delta^{13}C$ ‰. All CO_2-dominated gases display a narrower range spanning from –6.4 to +0.5 $\delta^{13}C$ ‰ and in this group the samples collected along the volcanic arc have still narrower range (-2.0 - +0.5 $\delta^{13}C$ ‰).

Considering the $\delta^{13}C(CO_2)$ values and the $CO_2/^3He$ ratios (Fig. 5), samples collected along the volcanic arc plot on the mixing line between the mantle and the limestones end-members. This pattern further excludes important contributions from organic sediments to the fluids deriving from the descending slab. A small contribution from organic sediments can be detected in the CO_2-dominated gases of mainland Greece deriving probably from crustal sources. On the contrary CH_4- and N_2-dominated gases display sometimes a strong organic contribution and low $CO_2/^3He$ ratios probably due to CO_2-depleting processes (carbonate precipitation, CO_2 reduction, etc.).

3.3 Geographical distribution

Measured R/R_a values of the Greek gas manifestations display an increasing trend going from north to south and from west to east (Fig. 6). A similar trend has been previously also evidenced by Shimizu et al. (2005) for the south Aegean volcanic arc. Based on the $^{87}Sr/^{86}Sr$ ratios of the least evolved rocks, they attributed this pattern to increasing crustal contamination of ascending magma.

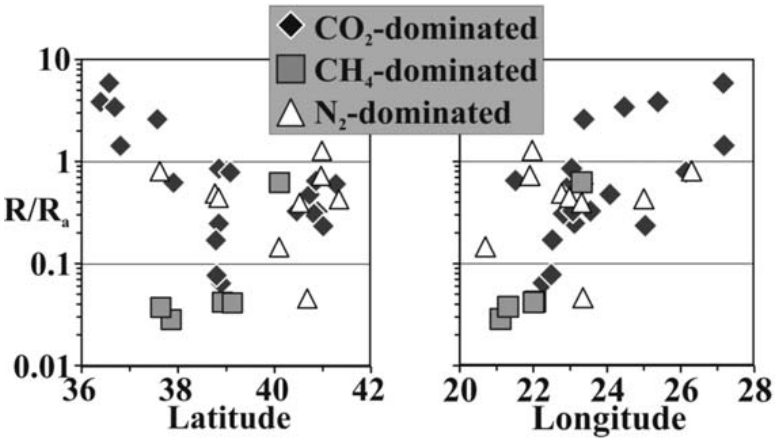

Fig. 6: Variation of measured R/R_a values of the Greek gas manifestations vs. latitude (left) and longitude (right) of the sampling site.

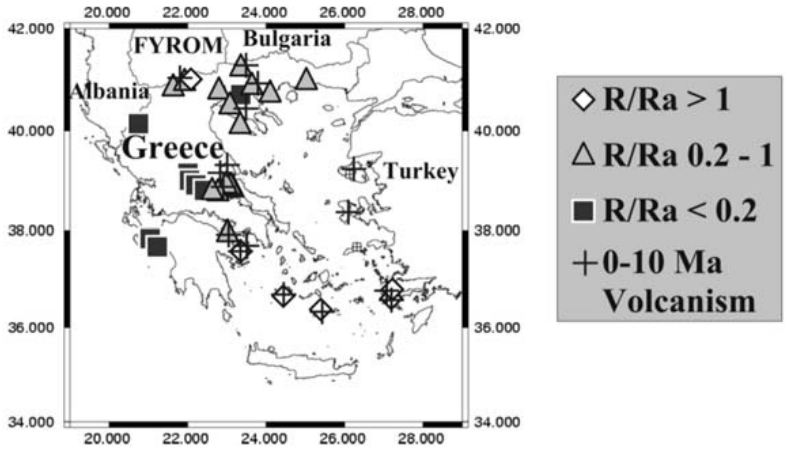

Fig. 7: Relationships between He isotopic compositions measured in the natural gases and the recent volcanic manifestations of the Hellenic territory.

Crustal contamination along the volcanic arc could be due to several processes. For example, Pe-Piper and Piper (2005) subdivided the arc in an older part comprising Methana and Milos and a more recent part comprising Santorini and Nisyros. Volcanism is considered to be slowly decreasing in the western sector, and the ascent of new magma from the mantle, being currently much lower than in the eastern part, supports a lower ^3He flux. A further significant difference between the eastern and western parts of the arc is in the type of volcanism. Santorini and Nisyros (in the east) are both characterized by central stratovolcanoes with large calderas and frequent eruptive activity during historical time (Pe-Piper and Piper, 2002). This volcanic environment facilitates the easy and rapid ascent of mantle fluids, and a corresponding lower probability of crustal contamination. In contrast, Methana and Milos (in the west) exhibit numerous monogenic centres accompanied by lower eruptive rates (Fytikas et al., 1986), which is compatible with a higher crustal contamination in the emitted fluids.

Gases with a clear crustal imprint in their He isotopic composition ($R/R_a < 0.2$) are found almost exclusively in the western part of Greece. In this area where the more external nappes of the Hellenide orogen crop out, the thickness of the crust reaches the highest values of the Hellenic region (> 40 km).

Gases with intermediate He isotopic composition (R/R_a 0.2 - 1) have been collected across the most internal terrains of the Hellenide orogen. In this area crustal thinning, due to extensive tectonics, favoured the recent (< 10 Ma) volcanic activity and either direct or magma-mediated mantle fluids ascent. This area is also the site of enhanced geothermal gradient (Fytikas and Kolios, 1979). Noteworthy almost all sites where gas samples with intermediate He isotopic composition (Fig. 7) have been collected fall close to recent volcanic centers and/or within the zones of highest geothermal gradient.

4. Conclusions

The 52 gas manifestations sampled along the whole Hellenic territory can be subdivided, on the basis of their chemical composition, in CH_4- N_2- and CO_2-dominated. The former two groups, almost all collected in the western part of the country, display also very low R/R_a values (< 0.2) highlighting their crustal origin. This region is characterised by a high crustal thickness (up to > 40 km) and absence of recent (< 10 Ma) volcanic manifestations. On the contrary samples collected in the eastern part of Greece, where instead the crust is thinner (20 – 30 km) and recent volcanic manifestations are widespread, the gases have generally CO_2-dominated composition and intermediate R/R_a values (0.2 – 1) evidencing a significant contribution from a mantle source. Finally, a strong mantle contribution was found in the samples collected along the south Aegean active volcanic arc, which all display a CO_2-dominated composition and high R/R_a values (1 – 5.8). CO_2 carbon isotopic composition and the $CO_2/^3He$ ratio of the latter gases evidence a mixing between a mantle and a limestone source excluding any contribution from sedimentary material. This is also confirmed by the measured N_2/Ar ratios, which are all close either to the atmospheric or to the air-saturated water ratio. A small contribution from sedimentary material, probably of crustal origin, can be highlighted in the CO_2-dominated gases of continental Greece.

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