# Gas geochemistry of shallow submarine vents in the Aegean sea (Greece)

Daskalopoulou K.[1-2], Longo M.[3], Calabrese S.[1], Gagliano A.L.[3], Kyriakopoulos K.[2], Italiano F.[3], D'Alessandro W.[3]

1) University of Palermo, Dept. DiSTeM, via Archirafi 36, 90123 Palermo, Italy

2) National and Kapodistrian University of Athens, Dept. of Geology and Geoenvironment, Greece

3) Istituto Nazionale di Geofisica e Vulcanologia – Sezione di Palermo, Via U. La Malfa 153, 90146 Palermo, Italy (walter.dalessandro@ingv.it)

The Aegean area, which is geodynamically very active, is characterised by intense seismic activity, presence of active volcanic systems and anomalous geothermal gradients. Like other regions of intense geodynamic activity it is also characterized by extensive geogenic degassing. Gas manifestations are not only widespread on land but are also very frequent underwater. Many of these, as for example those of Milos and Santorini, are known since long time and have been previously studied although the targets were generally the hot waters or the sediments affected by the emissions (Smith and Cronan 1978, Dando et al. 1995, Price et al. 2013, Megalovassilis 2014).

The present study aims at producing the first catalogue of the shallow submarine gas manifestations of the Aegean Sea and to characterize geochemically the emitted gases. To this end, 61 samples at 21 different sites have been collected by diving at depth between 1 and 15 m. Figure 1 shows the geographic distribution of the sampling areas and the UTM coordinates of the 21 sites are shown in Table 1. Most of the samples were collected along the south Aegean active volcanic arc (SAAVA) close to the coasts of Methana, Milos, Santorini, Nisyros, Gyali and Kos. The remaining samples have been collected at Evia, Kassandra peninsula and Samothraki.

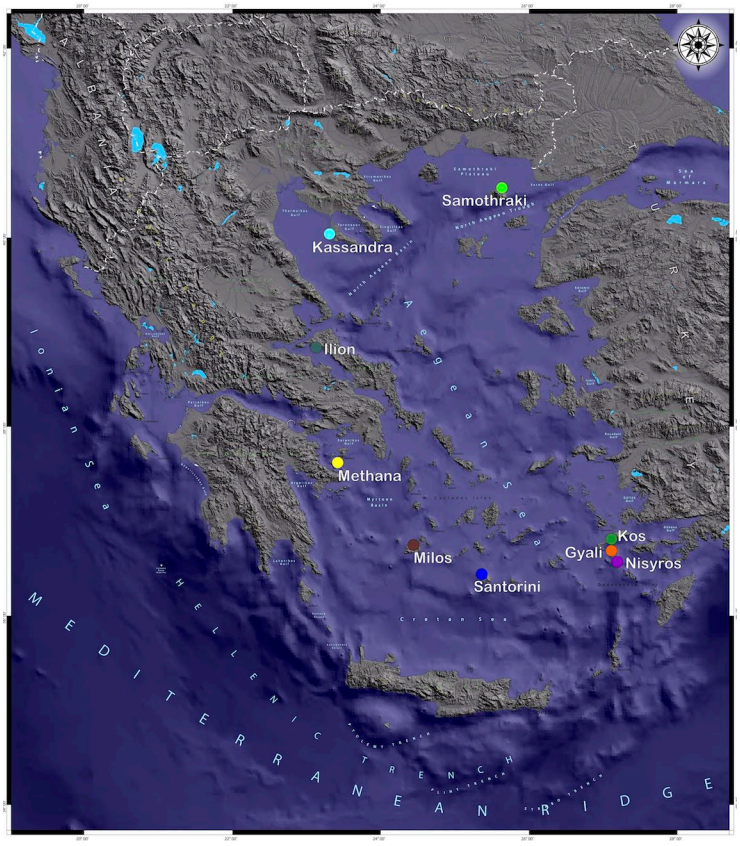



Fig. 1 – Geographic distribution of the sampling areas

Table 1 – Geographic coordinates of the sampling sites

| Area | Site | UTM coordinates (WGS84) | | |
|---|---|---|---|---|
| | | Sector | E | N |
| Evia | Ilion | 34S | 684788 | 4302532 |
| Kassandra peninsula | Ag. Pareskevi | 34S | 721293 | 4422552 |
| Kassandra peninsula | Xyna | 34S | 731638 | 4423292 |
| Samothraki | Therma Limani | 35T | 381584 | 4484685 |
| Methana | Pausanias | 34S | 708237 | 4168275 |
| Methana | Thiafi | 34S | 712355 | 4163870 |
| Milos | Paleochori | 35S | 272157 | 4068098 |
| Milos | Skinopi | 35S | 270211 | 4067712 |
| Milos | Adamas | 35S | 278078 | 4061694 |
| Santorini | Palea Kameni | 35S | 354725 | 4029380 |
| Santorini | Nea Kameni | 35S | 356561 | 4030695 |
| Nisyros | Katsouni | 35S | 517346 | 4051911 |
| Nisyros | Lies | 35S | 518202 | 4050287 |
| Gyali | Gyali | 35S | 511048 | 4057840 |
| Gyali | Gyali nord | 35S | 510958 | 4058232 |
| Gyali | Gyali west | 35S | 510511 | 4055549 |
| Kos | Bros Therma | 35S | 528308 | 4077682 |
| Kos | Paradise beach | 35S | 500794 | 4068393 |
| Kos | Kefalos | 35S | 497339 | 4065831 |
| Kos | Ag. Irini 1 | 35S | 520916 | 4075676 |
| Kos | Ag. Irini 2 | 35S | 521910 | 4075843 |

The sites displayed very different gas fluxes. Most of them showed a very sluggish gas bubbling while a few show strong bubbling over a larger area. The most intense manifestation was found at Kos Island along Paradise beach. There, in September 2016, a preliminary $CO_2$ flux survey was made with 12 measurements covering an area of about 250 $m^2$. Flux values ranged from 500 to 50,000 $g/m^2$/day from which a total output of about 3 tons/day has been estimated.

Gas samples have been analysed for their chemical (He, Ne, $O_2$, $N_2$, $H_2$, $H_2S$, $CH_4$ and $CO_2$) and isotopic (He, $CO_2$-C, $CH_4$-C, $CH_4$-H) composition by gas chromatography and mass-spectrometry methodologies. The chemical composition of almost all samples was dominated by $CO_2$ (Fig. 2).

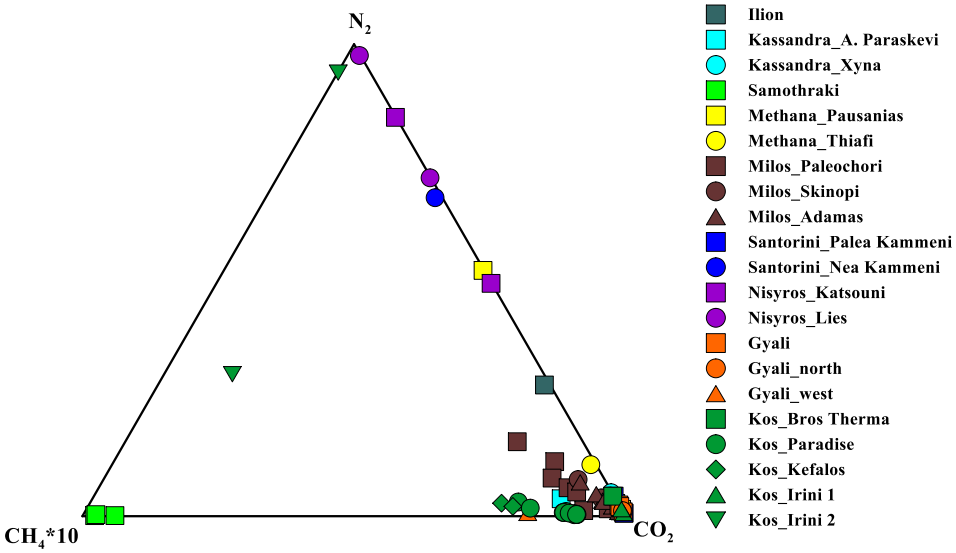



Fig. 2 – $CO_2$-$N_2$-$CH_4$ triangular graph

Only 11 samples, collected at very low flux vents, had $CO_2$ contents lower than 50%. Three of these samples derive from a $CH_4$-dominated reservoir (Samothraki) while the remaining show clear signs of $CO_2$ loss due to dissolution processes being sometimes highly enriched in less soluble gas species (He, $N_2$, $CH_4$). In one case (sample Irini2 of Sep. 2016) the dissolution process is so extreme that only 900 ppm of extremely fractionated $CO_2$ ($\delta^{13}C$ -20.1‰) is left over (Fig. 3). The helium isotopic composition, ranging from 0.74 to 6.73, points to a significant mantle contribution (5-95%) especially along the SAAVA (Fig. 4). Also the $\delta^{13}C$-$CO_2$ values (mostly between -5 and 0 ‰) indicate an important mantle contribution although $CO_2$ deriving from crustal limestones is often prevailing (Fig. 3).

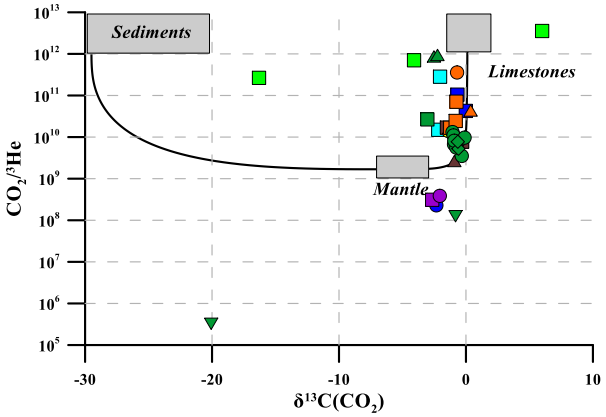



Fig. 3 – $CO_2/^3He$ vs. $\delta^{13}C$-$CO_2$

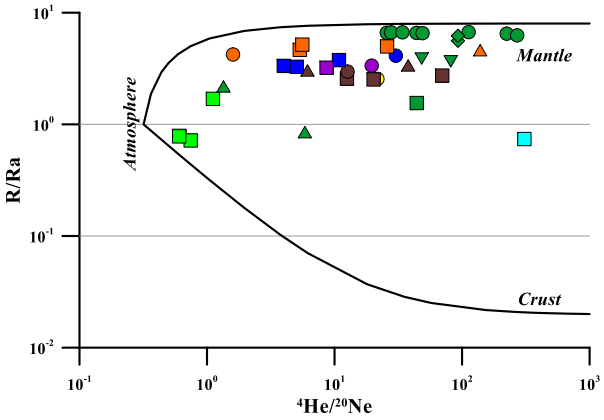
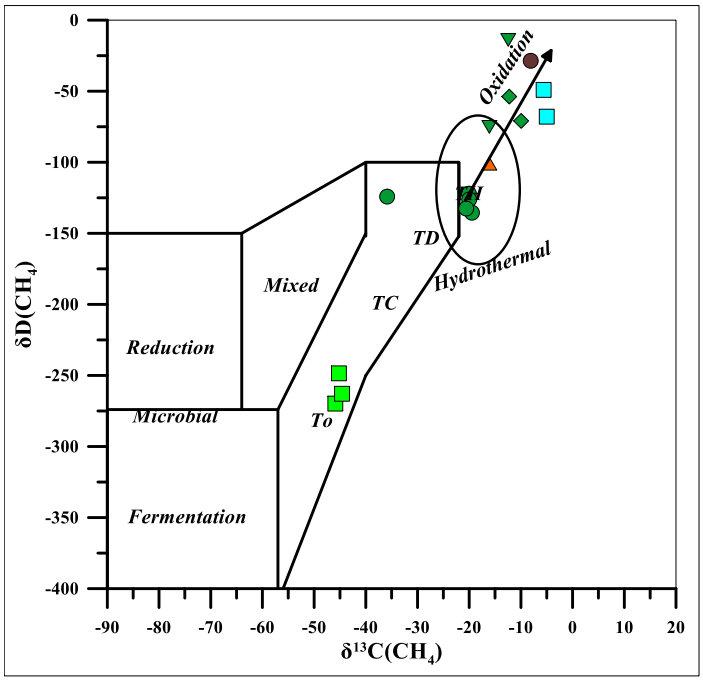


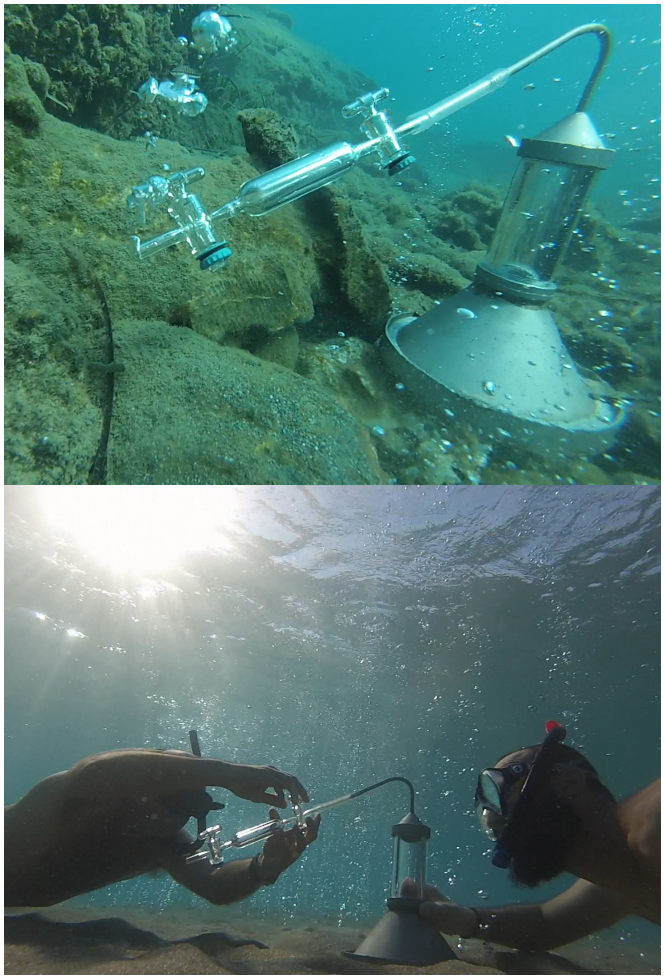

Fig. 4 – R/Ra vs. He/Ne

Isotopic composition of methane indicates mostly a hydrothermal origin either abiogenic or thermogenic (Fig. 5). Only the samples taken at Samothraki indicate a clear thermogenic origin (Fig. 5). Some sample shows more positive isotopic values pointing to possible biogenic methane oxidation processes.




Hydrogen sulphide, being highly soluble, was found only in three samples in concentrations ranging from 16 to 8200 ppm indicating a hydrothermal contribution.

Fig. 5 – $\delta^{13}C$ vs. $\delta D$ of methane



The present study highlighted a widespread submarine degassing activity in the Aegean Sea mainly along the active volcanic systems of the volcanic arc. The gas composition highlights their tight relationships with the volcanic and geothermal systems of the area. Gases from hydrocarbon fields are on the contrary rare. Although the gases emitted are sometimes quantitatively small they should not be disregarded because their environmental impact can be locally important. Furthermore these areas, especially those where nearly pure $CO_2$ is emitted, could be the sites where the impact on the marine environment of ocean acidification due to future increased atmospheric $CO_2$ levels or gas leakage from geologic $CO_2$ storage sites can be studied.

Fig. 6 - Underwater sampling at Methana and Gyali.

**Keywords**: submarine degassing, stable isotopes, environmental impact, ocean acidification

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