Scientific Diving Techniques Applied to the Geomorphological and Geochemical Study of some Submarine Volcanic Gas Vents 
(Aeolian Islands – Southern Tyrrhenian Sea – Italy)

G. Caramanna,1 N. Voltattorni,2 L. Caramanna,3 D. Cinti,2 G. Galli,2 L. Pizzino,2 And F. Quattrocchi2
1Via A. Soglio n. 79 00164 Roma (Italy)
2Fluid Geochemistry Laboratory - Italian National Institute of Geophysics and Volcanology
3Interuniversity Consortium – l.caramanna@caspur.it

Abstract

The Panarea Island lies few miles south of the active volcano of Stromboli (Aeolian Islands, Italy) in a very active hydrothermal area. On November, 4th, 2002 a huge submarine volcanic-hydrothermal gas burst was detected near the shoreline of Bottaro, an islet at around 1, 5 miles east of Panarea. The INGV Scientific Diving Team began the underwater surveys of the area from 5 to 40 meters below the sea surface locating a large field of gas vents. In two cases the high-pressure gas rising created sinkholes with the collapse of the seafloor. Scientific divers surveyed the area, took pictures, and collected samples of gas, hydrothermal springs water, and new-formation minerals. Customised SCUBA techniques were exploited and refined to collect these samples. Free and dissolved gases and water samples were analyzed by gas and liquid chromatographic techniques. The minerals, mainly of neogenic hydrothermal formation, were identified by X-ray-diffraction and by SEM. We deployed two data loggers to collect the hot vents temperature in long term period. The data collected suggest a correlation between the gas/water vents location/evolution and the main local and regional fault systems. The main component of the gas mixture is CO2 (up to 98 %) with presence of H2S, H2, CO, CH4 and He. What is still ongoing (September, 2004) has had a strong negative influence on the marine ecosystem. Discussed are the state of art of the methods, key-lines and the limits of the actual seabottom geochemical sampling as well as the possible future developments.

Underwater hydrothermalism in the Mediterranean Sea and Tyrrenian Sea

The Mediterranean Sea area is a geological active region with the subduction of the African plate under the European plate. Deep subduction basins (i.e. Marsili Basin) and volcanic arcs (i.e. Aeolian Islands are) lie in the south Tyrrhenian Sea as clues of the tectonic and volcanic activity. The active volcanism is believed to have begun in the Oligocene (Bellon, Jarrige et alii, 1979; Savelli, 1988). Actually active volcanoes are found along the Tyrrhenian shore (Vesuvio), in Sicily (Etna) and in the Aeolian Islands (Stromboli and Vulcano islands). The volcanic districts are located on the Benioff plane around 100-350 km above the focal depth of earthquakes (Ninkovich & Hays, 1972). Near the basins and the volcanic regions there is an increase of heat flow (up to 200 mW/m² in the Tyrrhenian abyssal plain) that coincides with gravity and magnetic anomalies (Dando et alii, 1999).

Close to the volcanoes there are geothermal active zones with gas vents (mainly CO2) and hot water springs both sub aerial and underwater (i.e. Naples Bay, Aeolian Islands). The total CO2 flow from the Mediterranean Sea gas vents is around 10⁷ – 10⁸ Kg/d comparable,
as magnitude order, with the total mid-ocean ridge vents that is $2.5 \times 10^8$ kg/d (Butterfield et alii, 1990; Italiano and Nuccio, 1991; Dando et alii, 1999).

The submarine vents detected are mostly in shallow water (less than 200 m depth) and bubble plumes are visible to divers, ROV and by echo sounder. In the neighboring areas bacterial mats and polymetallic sulfide deposits have been found (Marani et alii, 1997; Dando et alii, 1999).

There is a direct correlation between earthquakes, volcanic crisis and increasing of gas vents as numbers and flow. A reverse correlation has been detected between the gas flow and temperature and the sea tides (Dando et alii, 1999).

**Morphology of the hydrothermal field around the island of Panarea**

The Panarea Island lies few miles south of the active volcano of Stromboli (Aeolian Islands, Italy) in a very active hydrothermal area (Fig 1). Geochemical investigations around the island have revealed the presence of a large field of gas vents and warm water springs on the seafloor since the 1980’s (Italiano and Nuccio, 1991).

On November, 4th, 2002 a huge submarine volcanic-hydrothermal gas burst had been detected near the shore line of Bottaro, an islet 1,5 miles east of Panarea (Fig. 2).

An extensive survey of the new developed vents has been conducted by the Italian National Institute of Geophysics and Volcanology since then and is still on going.

The area delimitated by the islets of Dattilo, Bottaro, Lisca Bianca, Lisca Nera (Fig. 3) is characterized by a flat seabed, (lava layers, pebbles, gravel and sand) covered by Posidonia mats. The morphology is distinguished by banks, dykes and sub-circular depressions of some meters in diameter. There is a widespread presence of gas vents, often correlated with bacterial mats, aligned along the main regional and local faults (SW – NE, NW – SE, N-S). We suppose that the origin of the depressed circular shaped areas within the Posidonia mat, covered by sand, is associated with collapses of the seafloor due to ancient gas bursts. This opinion is supported by the actual presence of such phenomena other surveyed points (Fig. 4).
Near the islet of Dattilo, off the eastern shore, the seafloor lies at about 25 meters of depth with Posidonia matte. There are several closed circular areas with a sandy bottom and little gas vents. In one of these areas there is the Black Point vent. The name comes from the black colour of the fluids, due to the presence of metal sulphurs. Fluids came out from a fracture aligned NNE – SSW and covered by an outcrop of black metal sulphurs (Fig. 5). This is the hottest vent (130 °C) measured (Fig. 6). After March 2003 the black emission decreased and the fluid emission is mainly of gas and hot water.

Few hundreds meters away from the north point of the islet of Bottaro the seafloor, at 16 m of depth, is characterized by a flat sandy surface with some dykes. The gas rises through several linear emission sections aligned with a SW – NE trend (main group) and NW – SE with bacterial mats along the gas emission lines (Fig. 7). The gas emission is characterized by 3 – 5 second impulses of warm water. The maximum temperature of the fluids is around 35 – 40 °C (Fig. 6).
On the north of this area, at a distance of about 30 m, there is a collapsed sinkhole on the seafloor (Fig. 4). In this zone the seabed is represented by sand and big boulders. We suppose that the genesis of the sinkhole is due to the gas rising and consequent forming of a sort of cave just below the boulders. The collapse of the roof of the cave generated the sinkhole. The horizontal shape is sub-elliptical with the main axis aligned NNE – SSW and 7.5 m long. The secondary axis is NW – SE, 5.2 m of length. The seafloor of the area is 17 m deep, the sinkhole itself is 3 m deep. Around the boundary there is a cave about 2 m high and 3 m wide. On the bottom of the cavity lies a bacterial carpet. Bacteria filaments hang from the ceiling of the cave (Fig. 8). The structure is still in evolution and increasing in dimensions, due to the step collapse of the boundaries. Warm fluids rise from the bottom. From June 2003 to July 2004 the temperature increased from 34 °C to 90°C just few centimetres below the sandy bottom of the sinkhole (Fig. 6).

**Geochemistry of the gas vents**

More than 120 samples (both water and gas) have been collected from November 2002 up to December 2004. We performed an analysis in order to determine major and minor elements (liquid chromatography), trace elements (ICP-MS), dissolved gases in water and gases in the free phase (gas chromatography).

Obtained results were compared with data from literature (Italiano and Nuccio, 1991): water chemical composition showed an enrichment in Na-Cl and in trace elements (i.e., Li, As and Sr especially in the “black point”). This comparison suggested the hypothesis that sea water is locally affected by acid, reducing and more saline fluids that circulated at high.
temperatures in volcanic rocks. Figure 9 shows the Na-Cl enrichment in comparison with sea-water content: in particular, samples from May and July 2004 have the same content of samples collected just after the Panarea “crisis” (December 2002).

During the first months of Panarea “activity”, some vertical logs were performed: they showed the presence of convective cells with a mix of water and gas from the vents. Furthermore, they revealed a modification of pH from 8.0 to 5.0 and the redox variation from +80 mV to -200 mV probably due to the presence of H$_2$S.

Results from gaseous composition (mean values) is summarized in table 1: 98% of gases is composed by carbon dioxide. All the emission points have a methane content around 10 ppm excepting the “Black point” whose mean value is around 600 ppm. Figure 10 shows the direct relationship between temperature and CH$_4$ content in the “Black point” confirming the thermogenic origin of the methane. Discrete contents of helium (11 ppm) were found in every point. He isotopic analysis were carried out over 32 samples in order to define the origin of helium: the helium isotopic range is 4.1-4.5 suggesting a magmatic origin. Figure 11 shows the contemporaneous content variations of H$_2$ and H$_2$S inferring fractionation of gases by partial dissolution in water.

Gaseous composition of Panarea emission points is very different from literature. Data collected before November 2nd, 2002 have values typical of hydrothermal field while samples collected after the recent gaseous emission have concentrations typical of volcanic field suggesting an evolution of the system controlling Panarea emissions(Figure 12).

**Study methods**

Due to the presence of water we developed special techniques to adapt the usual sampling methods to the undersea environment.
Figure 10  CH₄/T in the “Black Point”

Figure 9  Na/Cl chart in the water samples
Figure 11 Variations of \( \text{H}_2 \) and \( \text{H}_2\text{S} \) inferring fractionation of gases by partial dissolution in water.

Table 1

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mean value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )</td>
<td>98 vol. %</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>10 ppm</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>0.4 vol. %</td>
</tr>
<tr>
<td>( \text{He} )</td>
<td>11 ppm</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>1100 ppm</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>2.2 vol. %</td>
</tr>
</tbody>
</table>

Figure 12 Ternary chart showing the volcanic composition of the gas samples in the area after the November 2002 crisis.
**Fluids sampling**

To collect free/dry gas samples we placed a plastic funnel upside-down (30 cm diameter with 12 kg ballast around the lower ring) exactly on the gas vent to be sampled. All the samplers are stored in a plastic box carried underwater by the divers (Fig. 13). The funnel is connected, through a silicon hose, to a Pyrex glass flask with twin valves. This flask has been previously filled with air, at a pressure higher than the hydrostatic pressure expected at the sampling depth, to avoid the sea water entering in the sampler. With this system we can change the flasks underwater to collect more samples at each vent. The same device is also used to collect the gas samples in NaOH 4 M filled flasks. In this case we fill the external section of the flask valve with distilled water to avoid sea water contamination.

![Figure 13 Underwater equipment used for the fluids sampling](http://archive.rubicon-foundation.org)

For the dissolved gas we used the traditional glass sampler filled with the water close to the vent. Radon gas is collected by the funnel linked to a cylindrical plastic sampler. In this case we fill the sampler with water and then we replace the water with the gas by placing the sampler upside-down on the gas stream coming out from the funnel.

Hot water sampling from the underwater springs is more difficult because of the low water flux and the need to avoid external seawater contamination. After several experiments our choice has been a glass flask with twin valves and vacuumed connected to a steel hose. Once the hose is fixed in the spring outlet we use a 60 cl syringe, connected by a 3 way valve, to expel the seawater from the hose and then fill the vacuumed flask just with the geothermal water. In this case there is less risk for seawater contamination.

**Helium hysotopes**

To collect gas for the helium hysotopes analysis we used a copper hose. On the extremities of the hose there are two steel clips designed to be closed by bolts and nuts. Once one of the extremities of the hose is connect to the funnel and the gas flows through we start closing the free extremity with a wrench. Then, just before disconnecting the sampler from the funnel, we close the other extremity. The use of a copper sampler assures that there is no lack of helium from the gas sample.
Temperature and sea level loggers
For a long term temperature-sea level data acquisition we deployed some STS data loggers near the main hot water springs. The logger is a full submergible cylindrical device (26 cm h, 2 cm diameter). The temperature range of the probe is -5 + 70 °C and the memory size is enough to store up to 130,000 measures. Scientific divers moored it on the seafloor by two steel sticks. To protect the sensor from the aggressive fluid we placed the logger in a plastic bag filled with fresh water and then in a plastic hose for mechanical protection. The data acquisition frequency is one measure per hour to correlate these data to the sea tides. Temperatures have also been collected by divers in each sampled vent by digital encased and glass thermometers.

Biological sampling
Close to the hydrothermal springs there are several mats of bacteria. To collect the bacteria we used 60 cc syringes with the needle section cut. With this device we aspirate the bacteria mat and, once in the boat, put the biological material in the refrigerator for further analysis.

Special diving techniques
The presence of aggressive fluids in the water (with a pH dropped from the usual 8 value of the sea to 5 or less closer to the vents) creates several problems.

The diver should not stay with their skin exposed to the gas for a long time. To avoid this in the longer sampling procedures we used full-face masks and dry suits to reduce the direct contact with the aggressive environment.

The metal parts of the diving gear (i.e. first stages of regulators, valves, cylinders, BCD connectors, zips etc.) undergo to a severe oxidation and need replacement or maintenance after few dives.

For extra safety and to improve data collecting we often used acoustic underwater communicators between the divers and the surface team.

Conclusions
The Panarea’s hydrothermal field shows clear correlations between the vents location and the local and regional faults setting. The system is still evolving with modification of temperature, gas composition and seafloor morphology.

The influence of the toxic gasses on the sea ecosystem is very strong with the disappearing of many benthonic life forms (i.e. death and dissolution of shells due to the low pH fluids), serious damage to the Posidonia mat and development of “anomalous” life forms like the sulphurbacteria.

The possible hazard is correlated to gas explosions on the seafloor and strong toxic gas emissions on the sea surface. The island of Panarea in summer is a very crowded holiday place and this can enhance the consequences of a volcanic crisis in the area.
Actually (December 2004) the whole system is still evolving but there are no signs of a dangerous increasing of the gas burst.

The aim of our survey is to create a model of the hydrothermal/volcanic system evolution. The data acquired by the data logger moored on the bottom of the sinkhole from 1st September 2004 to 17th November 2004 show a correlation between the warm water spring flow and the sea tide.

The *Bravais Pearson linear correlation coefficient* highlights a reverse correlation between daily sea tide and daily temperature of 0.95C. The explanation of this kind of correlation is that during the high tide the cold sea water is injected through the sand cover of the seafloor reducing the thermal flow of the vents.

The *simplified linear regression model* applied to the mean daily temperature data shows an increase of the temperature from September to October of 4.67 Celsius degree. In November there is a decrease of the temperature that should be correlated to the seasonal sea water temperature variation.

Other data will be necessary for an exhaustive study of the phenomenon but these first results show an evolution of the thermal field in good accordance with the geochemical outcomes. The development of special underwater fluid sampling techniques by scuba divers is another important result of this research project.

**Acknowledgments**

Dr. Alessandra Esposito that helped me in several dives. Thanks also to the National Italian Fire Brigade and the Italian Coast Guard

**Literature Cited**


Savelli C., 1988. Late Oligocene to recent episodes of magmatism in and around the Tyrrhenian Sea: implications for the processes of opening in a young inter-arc basin of intra-orogenic (Mediterranean) type. Tectonophysics 146, 163-181