

# ECO<sub>2</sub>

Sub-seabed CO<sub>2</sub> Storage:  
Impact on Marine Ecosystems



CRUISE REPORT ECO2-6  
(Panarea Island, Italy)  
October 19-31. 2012



Authors:

Stan Beaubien, Cinzia De Vittor, Annalisa Franzo

Citation: Beaubien S.E., De Vittor C, and Franzo A. (2012) Study of CO<sub>2</sub> flux, bubble behaviour and planktonic and benthic communities off Panarea Island (Italy): cruise report ECO2-6. Università di Roma La Sapienza, Roma, Italy / Istituto Nazionale di Oceanografia e Geofisica Sperimentale, Trieste, Italy 24 pp.

## Summary

1	Introduction.....	3
2	Objectives .....	5
3	Summary of Work .....	6
3.1	Participants .....	6
3.2	Narrative.....	6
4	Description of Work.....	8
4.1	Water column sampling (Basiluzzo Island).....	8
4.2	Sediment sampling (Basiluzzo and Panarea Islands) .....	9
4.3	Primary and secondary benthic production (Panarea Island) .....	10
4.4	Dissolved constituents flux (Panarea Island).....	11
4.5	Crater mapping (Bottaro Island).....	12
4.6	Gas bubble flux measurements (Bottaro Island) .....	13
4.7	Gas bubble behaviour experiments (Bottaro Island) .....	14
4.7.1	Bubble making .....	16
4.7.2	Bubble rise velocity measurements .....	17
4.7.3	Bubble size measurements .....	20
4.7.4	Chemistry of the gas and water column .....	21
5	Summary.....	22
6	Acknowledgements.....	23
7	References .....	24



Università di Roma “La Sapienza” - Centro di Ricerca  
“Previsione, Prevenzione e controllo dei Rischi Geologici”



ISTITUTO NAZIONALE  
DI OCEANOGRAFIA E DI GEOFISICA SPERIMENTALE

# 1 INTRODUCTION

Carbon capture and storage (CCS) is expected to provide an important, short-term approach for mitigating potential global climate change due to anthropogenic emissions of carbon dioxide (CO<sub>2</sub>). This technology involves the capture of CO<sub>2</sub> emitted from large point sources and its injection into deep geological reservoirs, such as depleted hydrocarbon reservoirs and deep saline aquifers, both on land and off-shore. Offshore reservoirs are particularly favourable due to potentially high storage capacities, the extra barrier provided by the overlying water, and the physical separation between injection sites and populated centres. The 14-year old Sleipner project, in the North Sea, is the world's first and largest pilot-scale CCS project; here about 1 million tonnes of CO<sub>2</sub> are injected per year into a deep saline aquifer

Despite the safe track record at Sleipner, several concerns exist amongst various stakeholders regarding the long term safety of sub-seabed CO<sub>2</sub> storage, including the potential for leakage of CO<sub>2</sub> and associated gases/compounds into the water column (with potential impacts on the marine ecosystem) and possible migration to the atmosphere. In addition, due to greater logistical problems, marine sites have been studied much less than terrestrial systems regarding site characterisation, monitoring, leakage detection and quantification, ecosystem impact, and human health and safety.

Although laboratory experiments and modelling can be performed, for a more complete (and realistic) understanding of a possible seabed leak of CO<sub>2</sub>, it is preferable to study natural, analogous systems. This is particularly important because CO<sub>2</sub> leakage presents some unique challenges. First, it is highly soluble and thus CO<sub>2</sub> bubbles will dissolve extremely rapidly; this makes bubble detection more challenging using hydroacoustic techniques. Second, dissolved CO<sub>2</sub> increases the density of seawater, and thus high CO<sub>2</sub> concentration seepage will likely remain closer to the seafloor.

Because of these complications, the Università di Roma "La Sapienza" and OGS first proposed the inclusion (within the ECO2 project) of the natural, shallow analogue site near the island of Panarea (Aeolian Islands, Italy; Fig. 1), where natural, thermo-magmatic CO<sub>2</sub> is leaking at substantial rates from the seafloor at water depths ranging from 5 to 30 m. This CO<sub>2</sub> is released most strongly in the area surrounding two of islets located 3 km to the east of Panarea (Lisca Bianca and Bottaro). This natural CO<sub>2</sub>-release field (c. 3 km<sup>2</sup>) has been active for centuries, with gas emanating from a

series of NW-SE and NE-SW trending fractures (Esposito et al., 2006). In the early 1980's researchers began to conduct gas geochemistry surveys of the area (Caliro et al., 2004), showing that the system was relatively stable in both gas chemistry (e.g. 98% CO<sub>2</sub>, 1.7% H<sub>2</sub>S plus other trace gases) and flux rates (7-9 x 10<sup>6</sup> l/d). On November 2 and 3, 2002, a gas outburst event increased the total gas flow rate by about 2 orders of magnitude (4 x 10<sup>8</sup> l/d) (Caliro et al., 2004), with large volumes of gas reaching the water surface. Flux rates began to decrease towards pre-outburst conditions about 3 months after the event. Most release points are gas only, although various points also release water of different origin, ranging from geothermal to seawater end-members that are mixed to variable degrees (Tassi et al., 2009).

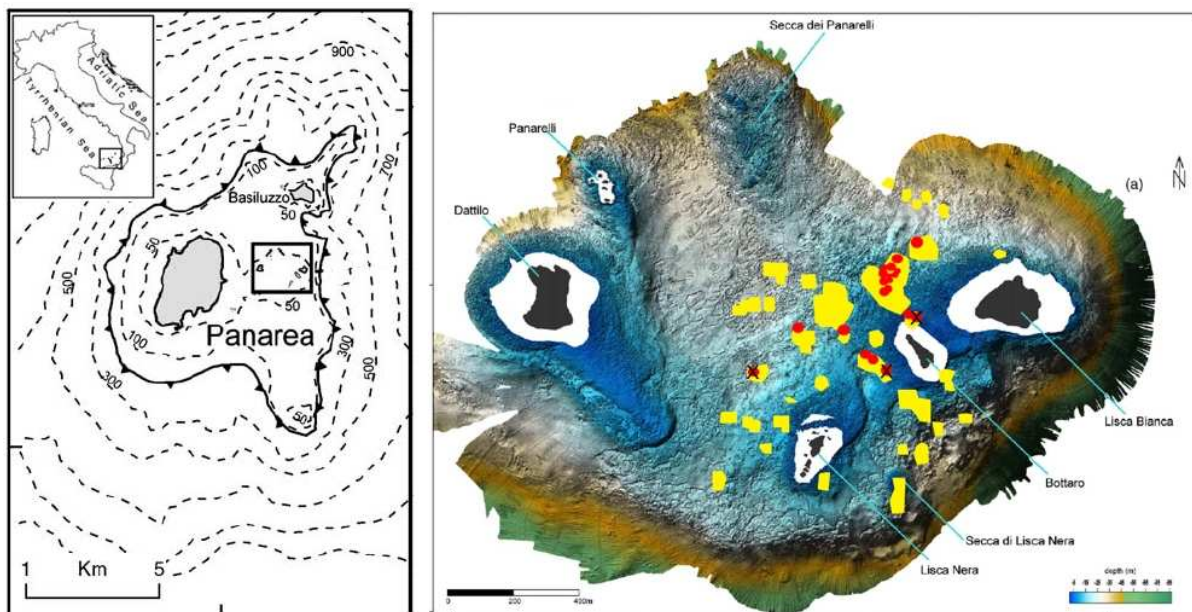


Figure 1. Map (left) showing Panarea Island and associated islets to the east (boxed area). Bathymetric map (right) showing the location of the gas leaks in December 2002 (yellow) soon after the outburst, the three strongest gas release points during the outburst (x), and the gas leak locations one year later (red circles). Modified after Esposito et al. (2006).

Based on the range of depths and relatively high and persistent gas flow rates, the occurrence of both gas only and gas-water seepage, and its close proximity to shore (Fig. 1b), Panarea represents an exceptional location to study natural processes and impacts related to shallow seabed CO<sub>2</sub> leakage.

The present report details work conducted at the Panarea site by UniRoma1 and OGS within the ECO2 project from October 19 – 31, 2012.

## **2 OBJECTIVES**

Research conducted at the Panarea site by UniRoma1 and OGS within the ECO2 project is within the framework of three separate work packages: WP2, WP3, and WP4.

WP2 is entitled “Fluid and Gas Fluxes across the Seabed at Storage Sites and Natural CO<sub>2</sub> Seeps”. The present cruise addressed the following specific goals related to WP2:

- Conduct gas bubble flux measurements using the accumulation chamber method, and combine these spatial and temporal results with mapping data to make an estimate of the overall leakage rate for a specific area.
- Perform benthic chamber measurements at sites where there is a flux of deep water which only contains dissolved CO<sub>2</sub> but no gas bubbles. The chamber was sampled for major and trace elements and carbonate system parameters. A pCO<sub>2</sub> probe was deployed within the chamber for continuous monitoring.

WP3, entitled “Fate of CO<sub>2</sub> and other Gases emitted at the Seabed”, focuses on the chemical, biological, and physical mechanisms that control CO<sub>2</sub> within the water column. Objectives of this field campaign related to this work package include:

- Study gas exchange processes between an ascending CO<sub>2</sub> bubble and the surrounding water column through the use of video filming, gas bubble chemistry analyses, and water column chemistry analyses.

WP4 is entitled “Impact of Leakage on Benthic Organisms and the Marine Ecosystems”, with research being focussed on biological aspects related to a CO<sub>2</sub> leak. Objectives of this campaign related to WP4 include:

- Water sampling to examine the effect of increasing pCO<sub>2</sub> on the planktonic ecosystem.
- Sediment sampling to determine impacts on benthic fauna (microphytobenthos and meiobenthos).
- Primary and secondary benthic production experiments in areas of fluid leakage.

### 3 SUMMARY OF WORK

#### 3.1 Participants

Family name	Name	Background	Institute
Beaubien	Stan	Geochemist	UniRoma1
De Vittor	Cinzia	Biologist	OGS
Ruggiero	Livio	Geologist	UniRoma1
Franzo	Annalisa	Biologist	OGS
Ingresso	Gianmarco	Biologist	OGS

#### 3.2 Narrative

##### October 19

- 20:00 Departure from Naples with the ferry bound for the Aeolian Islands

##### October 20

- 08:00 Arrival at Panarea
- 09:00 Unpacking, laboratory set-up, recovery of video structure
- 09:00 Modifications to video structure
- 15:00 Benthic chamber measurements off Panarea Island
- 17:00 Laboratory analyses

##### October 21

- 09:00 Modifications to video structure
- 09:15 Water column sampling at Basiluzzo Island
- 11:15 Water column sampling at Basiluzzo Island
- 15:00 Laboratory analyses

##### October 22

- 09:00 Modifications to video structure
- 10:00 Laboratory analyses
- 11:45 Video mapping of crater off Bottaro Island
- 13:20 Gas bubble flux measurements off Bottaro Island
- 14:00 Gas bubble behaviour experiments off Bottaro Island
- 16:00 Sediment sampling off Basiluzzo Island

##### October 23

- 13:30 Gas bubble behaviour experiments off Bottaro Island
- 14:30 Deployment of pCO<sub>2</sub> probe

##### October 24

- 10:40 Video mapping of crater off Bottaro Island

- 13:00 Water column sampling
- 14:30 Gas bubble behaviour experiments off Bottaro Island
- 17:00 Laboratory analyses

#### October 25

- 09:30 Sediment sampling off Panarea Island
- 09:30 Primary and secondary benthic production experiments
- 09:30 Benthic chamber measurements off Panarea Island
- 16:30 Testing of video structure
- 16:30 Gas bubble flux measurements off Bottaro Island
- 18:00 Laboratory analyses

#### October 26

- 12:30 Gas bubble behaviour experiments off Bottaro Island
- 13:00 Deployment of pCO<sub>2</sub> probe
- 15:00 Water column sampling
- 17:00 Laboratory analyses

#### October 27

- Rough seas
- Data analysis
- Laboratory analyses

#### October 28

- Rough seas
- Data analysis, cleaning and packing of equipment

#### October 29

- Rough seas
- Data analysis, cleaning and packing of equipment

#### October 30

- 15:00 Took ferry to Milazzo, drove to Messina, then took ferry to Salerno

#### October 31

- 09:20 Arrival at the Port of Salerno

## 4 DESCRIPTION OF WORK

### 4.1 Water column sampling (Basiluzzo Island)

Two stations, located just off the eastern tip of Basiluzzo Island and defined during the ECO2-4 cruise of June 2012 in accordance our ECO2 colleagues MPI/Hydra, were sampled during this cruise:

- station B1 (38°39.749' N, 15°07.132' E), characterized by gas emission
- station B2 (38°39.827'N, 15°07.118'E) without gas emission, referred to as the control site.

The physical characterization of the water column was performed using a CTD (SeaBird 19 plus) equipped with the sensors described in Table 1. These sensors are calibrated on a regular basis in the OGS calibration laboratory.

*Table 1. Technical characteristics of the sensors mounted on the CTD probe.*

PARAMETER	RANGE	ACCURACY	RESOLUTION
Temperature (°C)	-5 to 35	0.005	0.0001
Conductivity (S/m)	0 to 9	0.0005	0.00007 S/m (resolves 0.4 ppm in salinity)
Pressure (strain gauge)	0 to 100	0.1% of full scale range	0.002% of full scale range
Fluorescence (Scufa submersible fluorimeter)	4 orders of magnitude		12 bit
pH (SBE18)	0-14 pH	0.1 pH	
Dissolved Oxygen (SBE43)	120% of surface saturation	2% of saturation	

The resultant CTD data, which defines water column stratification and pH distribution, was used to choose the depth of discrete water samples (at three levels) for various chemical and biological analyses, including: dissolved oxygen, pH, alkalinity, dissolved inorganic nutrients, dissolved organic phosphorous and nitrogen, particulate total carbon, particulate organic carbon, dissolved gasses and H<sub>2</sub>S concentration, phytoplankton abundance and diversity, microzooplankton abundance and diversity, heterotrophic nanoplankton abundance and diversity, and prokaryote abundance. The rates of prokaryotic carbon production and the exoenzymatic activities have also been examined.



All samples were placed in coolers with ice packs on the boat until transfer to the land laboratory on Panarea Island. Samples for oxygen, pH and exoenzymatic determination were immediately analysed, while those for particulate organic and inorganic matter were filtered and filters were frozen until return to the laboratories at OGS. Samples for prokaryotic carbon production were pre-processed and stored until the determination of their activity by a  $\beta$ -counter (Packard Tri-Carb 2900TR) at the OGS laboratories.

#### 4.2 Sediment sampling (Basiluzzo and Panarea Islands)

Sediment samples were collected for the analyses of abiotic parameters (sediment grain-size, Total Organic Carbon, Biopolimeric Carbon) and benthic communities (picobenthos, microphytobenthos and meiofauna). A total of five stations were sampled: three near Basiluzzo Island previously identified with our ECO2 colleagues MPI/Hydra (station B1, “Red with Gas” - 38°39.749’N, 15°07.132’E; station B2, “Grey no Gas” - 38°39.827’N, 15°07.118’E; and station B3, “Grey with Gas” - 38°39.82’N, 15°07.137’E), and two just NE of Panarea Island (38°38.536’N, 15°04.714’E) where the sediments are characterized by very different temperatures at a distance of approximately 1 m one from another. This last site is referred to here as “Hot-Cold” (HC) and by partners MPI-Hydra as site “Corpi Morti.



Figure 1. Sampling of sediment by scuba diver (a); extrusion of sediment cores and surface layer subsampling (b)

Virtually undisturbed sediment cores were collected by scuba divers using cut-off plastic syringes (2.7 cm i.d., length 11.4 cm) and then the lowermost side was closed

with a plastic cap (Figure 1a). Samples of abiotic parameters, picobenthos and meiofauna were collected in triplicates and immediately stored at  $-20^{\circ}\text{C}$  until subsequent processing in the OGS laboratories. For chemical analyses, the sediment cores were partially extruded and only the surface layer (1 cm thick) was collected (Figure 1b). For microphytobenthic analyses the surface sediment layer was fixed with 4% formaldehyde/filtered sea water and stored at  $4^{\circ}\text{C}$ .

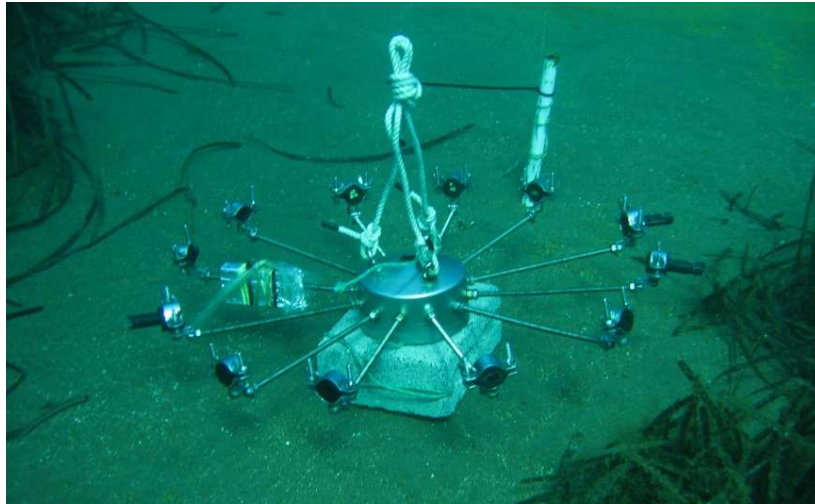
### **4.3 Primary and secondary benthic production (Panarea Island)**

Primary and secondary benthic production were measured at the two sites off Panarea Island where the other benthic parameters were collected.

Primary Production (PP) was estimated using the  $^{14}\text{C}$  incubation method. Two sediment cores were collected at each site by scuba divers using cut-off plastic syringes (2.7 cm i.d., length 11.4 cm). The surface layer (0.5 cm thick) was extruded and re-suspended in 100 mL of previously filtered ( $0.2\ \mu\text{m}$ ) in situ sea water. After inoculation of 500  $\mu\text{L}$  of  $\text{NaH}^{14}\text{CO}_3$  (10  $\mu\text{Ci}$ ), 9 mL of the slurry was transferred into 9 glass vials divided as follows: 3 replicates to assess the sediment matrix effect, 3 dark replicates and 3 light replicates. Carbon incorporation was immediately stopped in the first 3 vials adding 100  $\mu\text{L}$  of  $\text{HCl}$  (5N). The other vials were incubated in situ for 1 hour (Figure 2). At the end of the incubation period, carbon incorporation was stopped in all vials. PAR measurements were performed at the beginning and at the end of both incubations.

Secondary benthic production was measured using the incorporation of  $^3\text{H}$ -Leucine (Leu). As for PP, two sediment cores were collected at each site by scuba divers using cut-off plastic syringes. The surface layer (0.5 cm thick) was extruded and homogenized. Aliquots of 200  $\mu\text{L}$  were subsampled in 5 plastic vials (2 controls and 3 replicates). After the addition of  $^3\text{H}$ -Leu (6  $\mu\text{Ci}$ ) to all the subsamples, the radiotracer incorporation in the controls was stopped by adding 80% ethanol (1.7 mL) while the other vials were incubated in situ for 1 h together with samples of PP. After incubation, 1.7 mL of 80% ethanol was added to the incubated vials.

The samples of PP and PCP were stored at  $4^{\circ}\text{C}$  until the subsequent processing at the OGS laboratories.

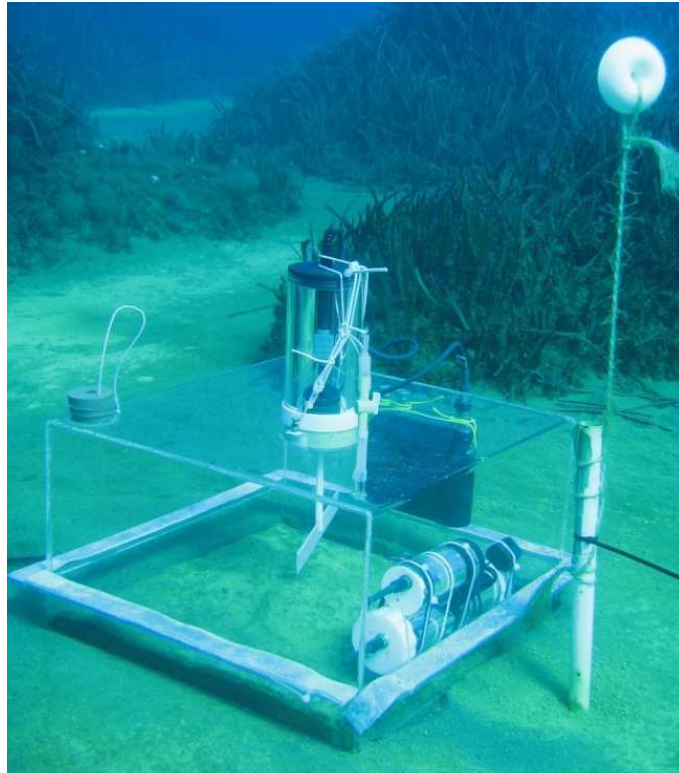


*Figure 2. Rosette for the in situ incubation of primary and secondary production.*

#### **4.4 Dissolved constituents flux (Panarea Island)**

The benthic chamber experiments were conducted at the Hot-Cold (Corpi Morti) site described above (38°38.536'N, 15°04.714'E), where small areas (c. 1-2m in diameter) of hot sand are surrounded by normal temperature sediments. The benthic chamber was used to measure the flux of dissolved CO<sub>2</sub>, heat, various carbonate system parameters, and major and trace elements from the sediments to the overlying seawater. Two points were measured that are located only 1m from each other, one having hot sediments the other cold. Measurements were made on the assumption that the hot sediments are an indication of deep, hydrothermal waters that are migrating to the surface via preferential pathways.

The experiments were conducted as follows. First a pCO<sub>2</sub> probe was placed on the cold measurement point and left for 10 minutes to equilibrate with the surrounding conditions. After this period, water samples were collected from right beside the probe, just above the sediments, and then the benthic chamber was placed over probe (Figure 3). Samples were then collected from the chamber 3 times (once every 10 minutes) and then the probe was moved 1m to the hot site to repeat the procedure. Collected water samples will be analysed for dissolved inorganic carbon (DIC), dissolved oxygen, hydrosulfide, pH, dissolves gasses, anions and cations. In addition, another two different hot spots were also measured with the benthic chamber, however only using the pCO<sub>2</sub> probe (i.e. no samples were collected for analysis).



*Figure 3. Benthic chamber deployed at the hot sand site at the Corpi Morti. Note the  $p\text{CO}_2$  sensor deployed within the chamber, with an external pump to maintain flow onto the probe membrane to decrease response time.*

#### **4.5 Crater mapping (Bottaro Island)**

As the area known as the “crater” was chosen as a central site around which various experiments would be conducted, it was decided that this morphological structure should be mapped. As a first overview of the site, videos were made of the crater by pointing the camera vertically downwards and swimming a series of parallel lines at two different heights, one from about 3 m above the sediment floor and another from the water surface about 12 m above the sediments (Figure 4). Video processing will involve exporting still photographs from the video (for example one every 30 frames) and then merging them together using a digital photography software package. This final image, at both heights, will then be combined with hand-drawn maps made by the divers to produce a detailed overview of the site’s morphology and gas leakage distribution, needed for estimating the total gas bubble flux (see below).

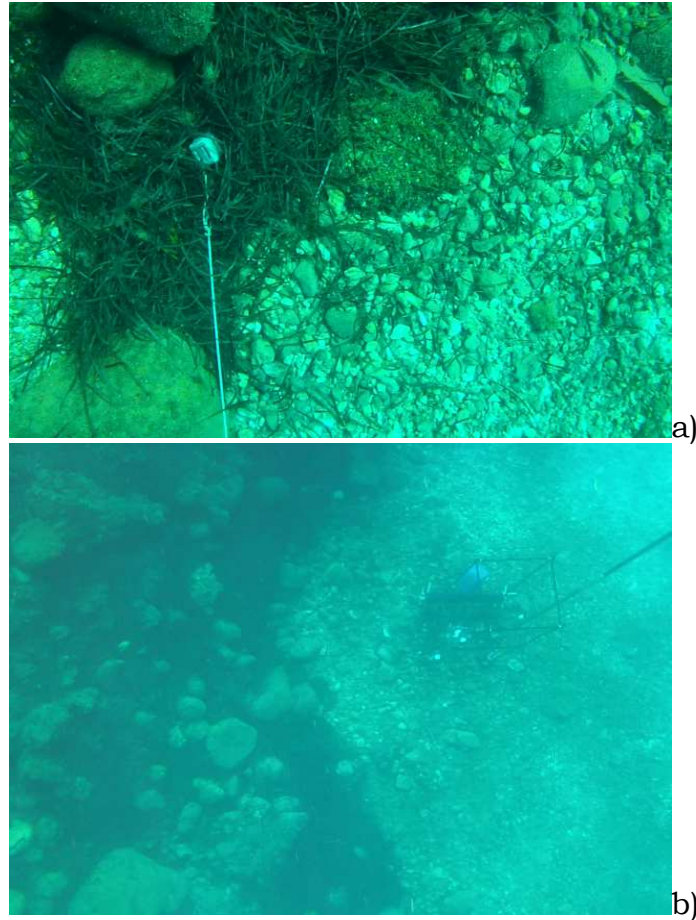


Figure 4. Single screen captures of the two videos conducted for mapping of the crater area: a) from a height of about 3m and b) from the water surface (c. 12 m height). Note the video support structure in photo (b).

#### **4.6 Gas bubble flux measurements (Bottaro Island)**

The mapping of the crater area has defined a total of 3 sub-zones that have a similar type of gas leakage rate: i) very high point flux (typically along the crater border); ii) high diffuse flux; and iii) low diffuse flux. Four representative points were picketed to facilitate repeat sampling. The flux rate at each point was measured using a funnel and a graduated accumulation chamber (Figure 5). The average flux rate calculated for the 4 points within each sub-zone will then be applied to the surface area of that sub-zone, and then the total flux from each of the three sub-zones will be added to estimate the total flux from the crater itself.

During this campaign the 12 points were measured on 2 separate occasions, with the duplicate flux rates measured for each point being within about 20-30% of each other.



Future campaigns will re-sample these same points, with measurements being conducted during low and high tide to see if the tides influence the gas flux rates at this site (as observed at the Basiluzzo site by various ECO2 partners).

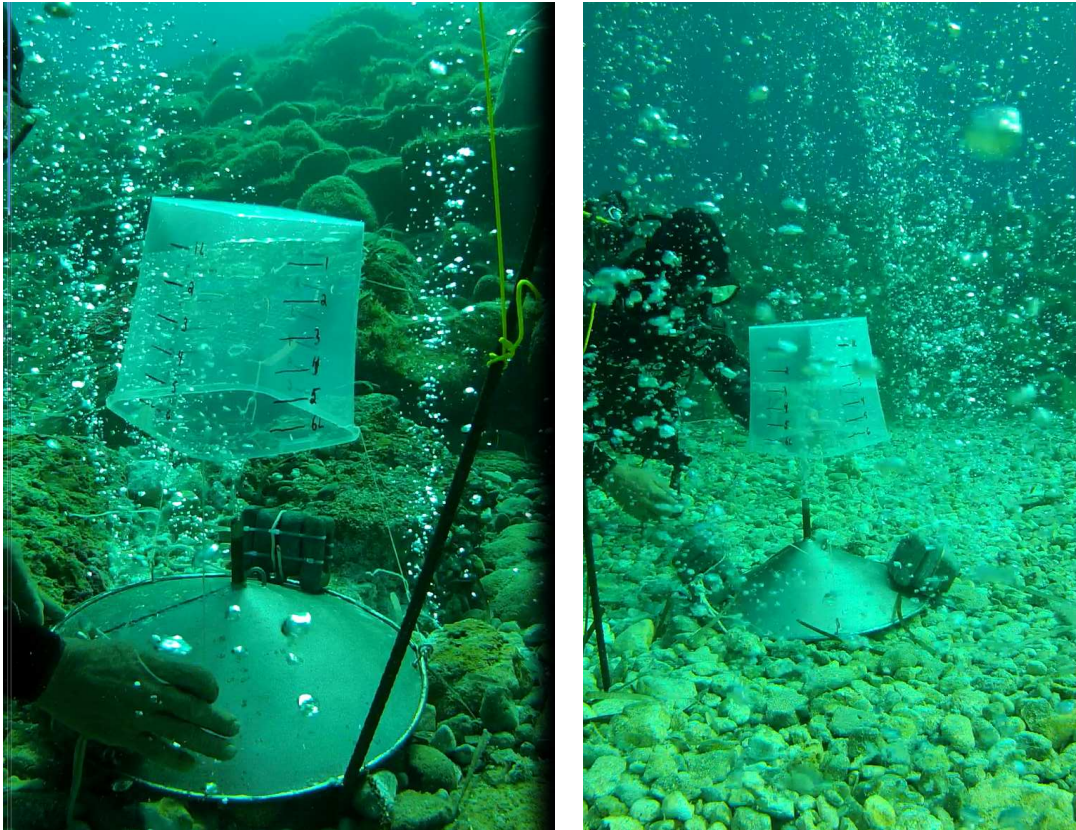
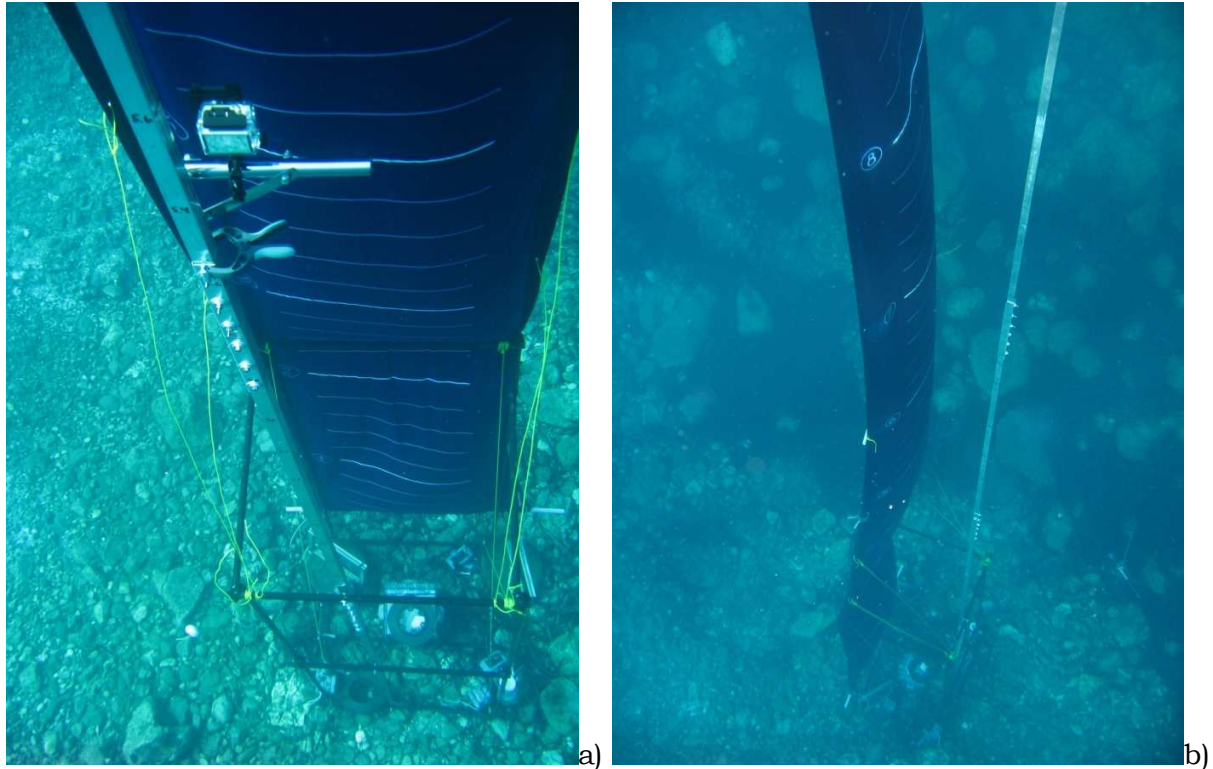


Figure 5. Large metal funnel and graduated accumulation chamber used for measuring the gas bubble flux rate at a low (a) and high (b) flux site.

#### **4.7 Gas bubble behaviour experiments (Bottaro Island)**

An important goal within the ECO2 project is to better understand the fate of CO<sub>2</sub> in the water column after it has migrated out of the sediments. As a CO<sub>2</sub> bubble rises it will exchange gases such that CO<sub>2</sub> dissolves into the water and N<sub>2</sub> and O<sub>2</sub> are stripped out of the water into the bubble. These processes, combined with such factors as depth (i.e. confining pressure), temperature, and salinity, will control the life of the bubble and how it evolves in size and composition during its ascent. Once dissolved in the water, the CO<sub>2</sub> can then be transported via currents, react chemically or biologically, or can eventually be released to the atmosphere.

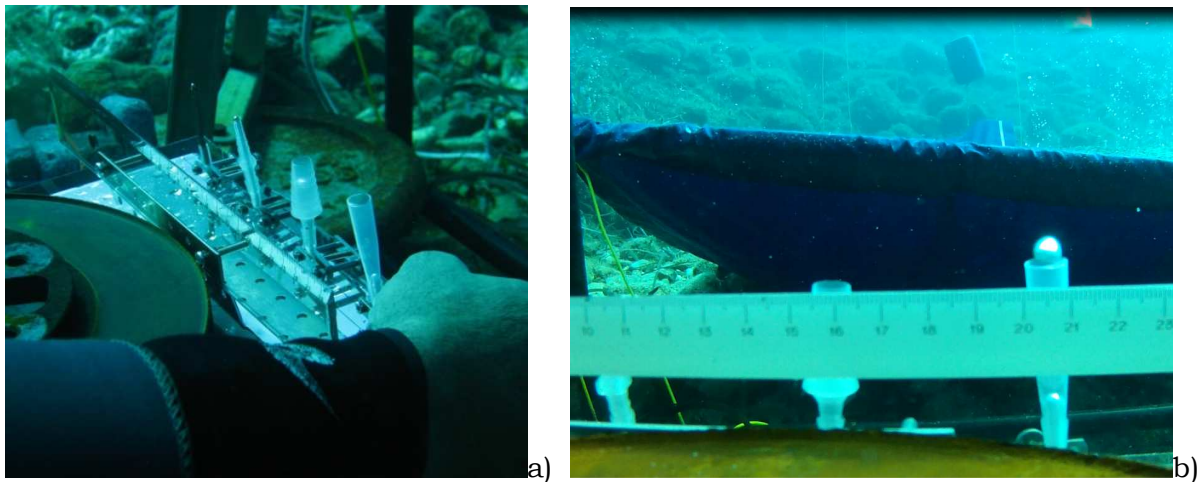


*Figure 6. Views of the bubble filming structure: (a) from a height of about 5m looking down with the video camera mounted on the track and (b) from higher up showing about 8.5 m of the structure and how the background cloth and camera track extend well above the original 3m structure.*

Experiments were conducted during the present campaign to address such issues, building on the experience gained during the testing phase conducted in August of this same year (Beaubien and De Vittor; 2012). Issues related to camera type, camera guide, support structure, and bubble type highlighted during that previous work were all taken into consideration for the present study, while at the same time the scope of the work was enlarged to encompass all aspects needed to understand bubble behaviour. This included the collection of gas bubbles and water samples at different heights to monitor chemistry changes along the ascent pathway, performing CTD profiles to determine salinity and temperature along the vertical profile, deploying  $p\text{CO}_2$  sensors for the duration of the experiment to monitor temporal changes in dissolved  $\text{CO}_2$  concentrations, and testing a new system for measuring the size of the bubbles at different heights along the flow path.

#### 4.7.1 Bubble making

As observed in the previous campaign (Beaubien and De Vittor; 2012), there were limitations with using natural bubbles leaking from the sediments as study subjects, first because it limits the choice of sites where work can be conducted (often to locations where it was difficult to set up the support structure) and second because the actual size and volume of the bubbles was unknown.



*Figure 7. Close up view of the bubble making device, with all four tubes making different sized bubbles (a) and only the largest tube in operation with a better marked ruler for scale (b). Each bubble tube has its own valve which can be used to regulate flow.*

To overcome these problems a simple device was constructed which would allow the capture of the gas leaking from the sea floor and to use it to produce different sized bubbles at any desired location. The device is a Plexiglas box with 4 tubes of different sizes on the top, each of which has a valve which is used to regulate flow (Figure 7a, b; Figure 8a). A ruler is also placed in front so that bubble diameter at the moment of release can be estimated. Although all 4 bubble sizes were initially studied together, it was difficult to identify the different bubbles once the video camera had moved vertically upwards. As a result, all subsequent experiments were done with 3 tubes closed and one open to produce bubbles of a single size.

As can be seen in Figure 8a, a floating barrier was placed within the box to physically separate the gas from the water. This was done to eliminate (or at least minimise as much as possible) the exchange of gas between the free and dissolved phases. Without



this barrier CO<sub>2</sub> could dissolve into the water and O<sub>2</sub> and N<sub>2</sub> could transfer into the gas phase, thus changing the chemical composition of the bubbles over time.

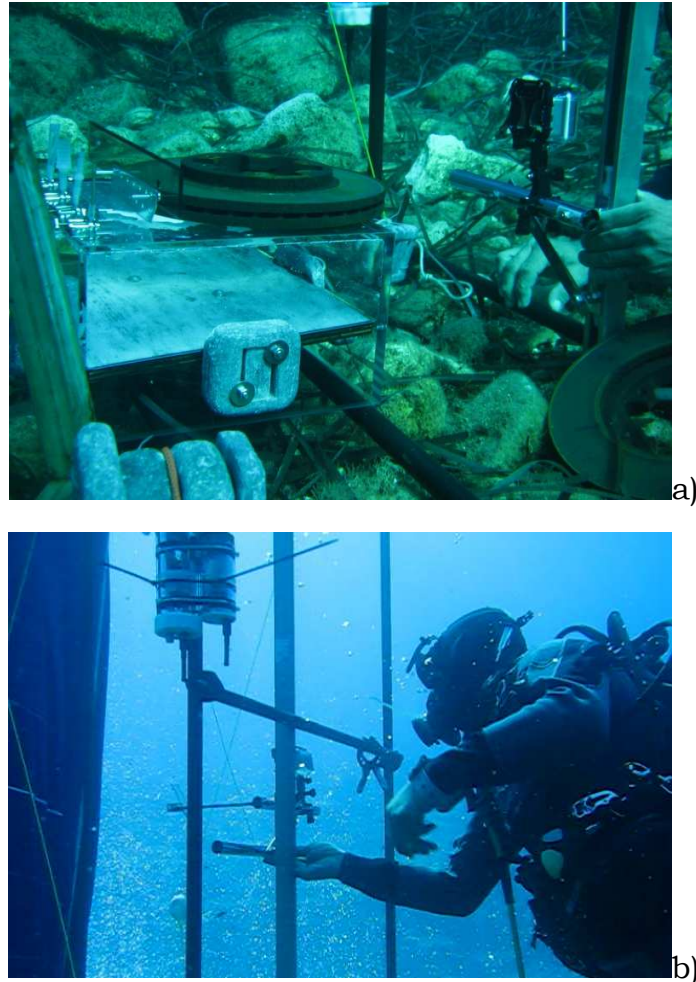
#### **4.7.2 Bubble rise velocity measurements**

The measurement of bubble rise velocity has been conducted by filming the ascent of individual bubbles with a video camera pointing horizontally. The dark blue cloth provides a uniform backdrop for excellent contrast while the horizontal lines every 20cm provide a spatial reference system. By measuring the time it takes a bubble to rise over each 20cm interval, a graph can be constructed of “semi-instantaneous” velocity versus travel distance.

As has been outlined previously (Beaubien and De Vittor; 2012), the first design for these measurements was cumbersome and prone to blocking. Two things were changed in this version to address these issues.

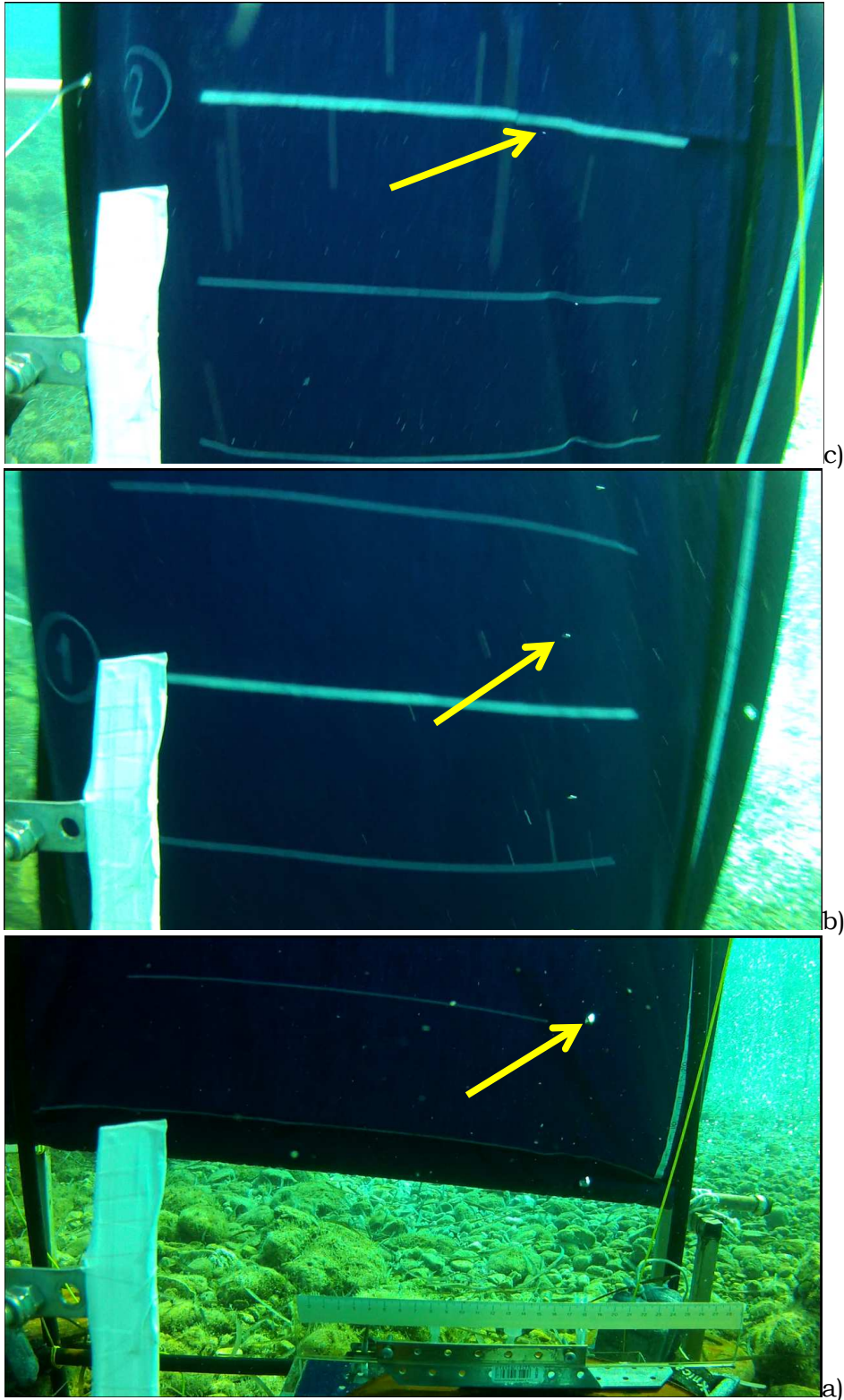
First underwater video camera was changed, from a large bulky unit to a much smaller more specialized camera. This latter, shown in Figure 8, is the GoPro Hero2 model, a very compact camera developed for use in extreme sports. This camera is capable of taking high resolution video and 11 megapixel still photos, and with the addition of an underwater filter contrast is high and colours are closer to reality. The very small size also means that it is easier to mount and to move underwater.

Second the camera support and guide has been completely re-designed. Instead of the two horizontal bars that slide along the main structure, as used the last time, four 2.5m-long tracks were mounted in series to provide a 10m long vertical support along which the camera could be moved (Figure 6b; Figure 8a, b). Although these tracks and the guides that slide within them are actually sold for the mounting of horizontal sliding doors, their use in this application was quite successful.



*Figure 8. Scuba diver operating the video camera on the support structure, at the base near the bubble making device (a) and at about 1.5 m height (b). Note the pCO<sub>2</sub> probe mounted on the structure in the upper left of (b).*

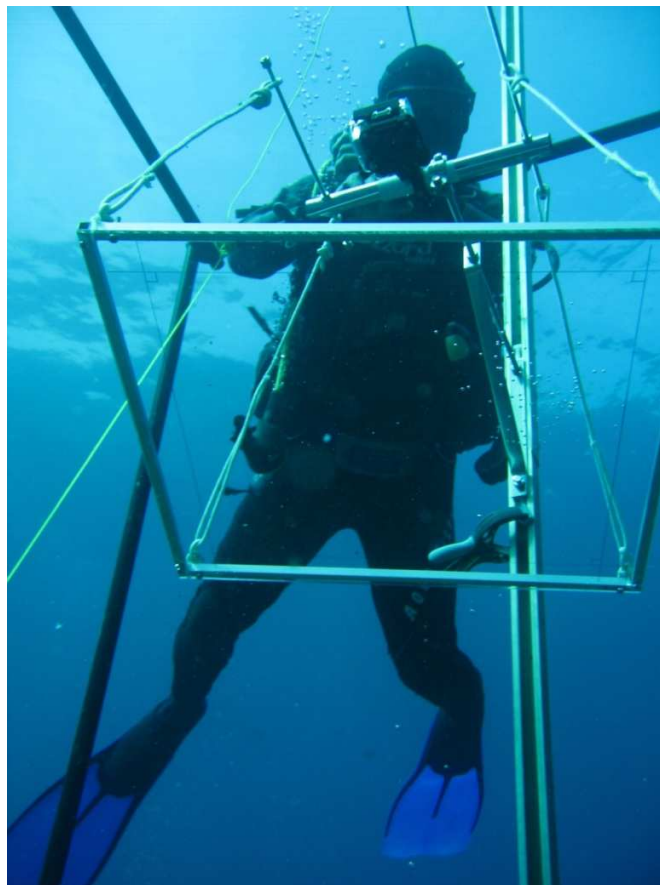
A series of measurements were made. On the first day the video camera was fixed at 40cm height intervals to record the bubbles as they passed at each height. This was done with all four bubble tubes open, however as noted above it was difficult to identify the origin of each bubble once the camera had move up about 80cm. On the second and third days only the largest bubble tube was opened and the camera was instead moved along the track vertically to follow the bubbles as they rose. An example is given in Figure 9, where a series of frames from a video were chosen to show how a bubble changes during its ascent. From its release at the base Figure 9a, the approximately 8mm diameter bubble rapidly shrinks until it is almost no longer visible at 2m height (Figure 9c).



*Figure 9. Screen captures from one experiment showing how bubble size decreases moving up the water column, from the sediments (a) up to 2m (c). The yellow arrows mark the same bubble; note that by about 2m this bubble has almost completely disappeared.*

### 4.7.3 Bubble size measurements

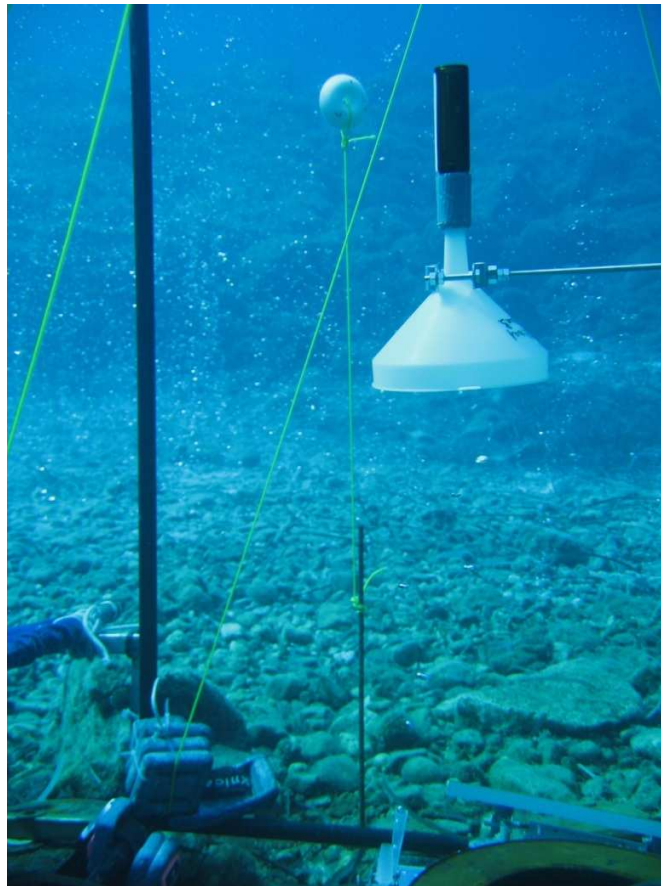
Given that a horizontal video is unable to accurately measure the bubble diameter due to the potentially variable distance between the bubble and the camera, a different methodology had to be developed which used a fixed reference distance. The chosen approach uses a clear Plexiglas sheet suspended 40cm below the vertically downward looking video camera (Figure 10). With centimeter squares marked on the Plexiglas and the constant distance, a stable reference system was created. Examining the video data frame by frame, it is possible to stop a bubble immediately before it touches the Plexiglas and measure its diameter. Measurements were made with the Plexiglas at 40, 80, 120, 160, and 200cm heights.



*Figure 10. Scuba diver taking video footage of the bubbles rising and hitting the Plexiglas sheet, used to measure the bubble size at a given height.*

#### 4.7.4 Chemistry of the gas and water column

As a CO<sub>2</sub> bubble rises through the water column there is an active exchange of gas between it and the surrounding water column, with CO<sub>2</sub> dissolving into the water and O<sub>2</sub> and N<sub>2</sub> being stripped into the bubble. This process depends on a series of physical and chemical parameters (e.g. bubble surface area, water temperature and salinity, dissolved gas concentrations, etc.) which must be measured to define the environmental parameters needed to model the observed bubble behaviour.



*Figure 11. Funnel and glass vial used to capture the rising bubbles at a given height for chemical analyses.*

To measure the changes in bubble chemistry along the flow path, samples were collected by mounting an inverted funnel with an attached glass VOA bottle (Figure 11) at the same height intervals used to measure the bubble diameters (see Section 4.7.3 above). Once brought to surface the samples were transferred with a syringe into pre-evacuated stainless steel canisters for transport back to the lab for analyses.



To measure the chemistry along the water column in the exact location of the vertical profile, divers were used to carry the CTD (Figure 12a) and to hand-trigger 5L Niskin bottles at the chosen depths (Figure 12b) along the edge of the video support structure.

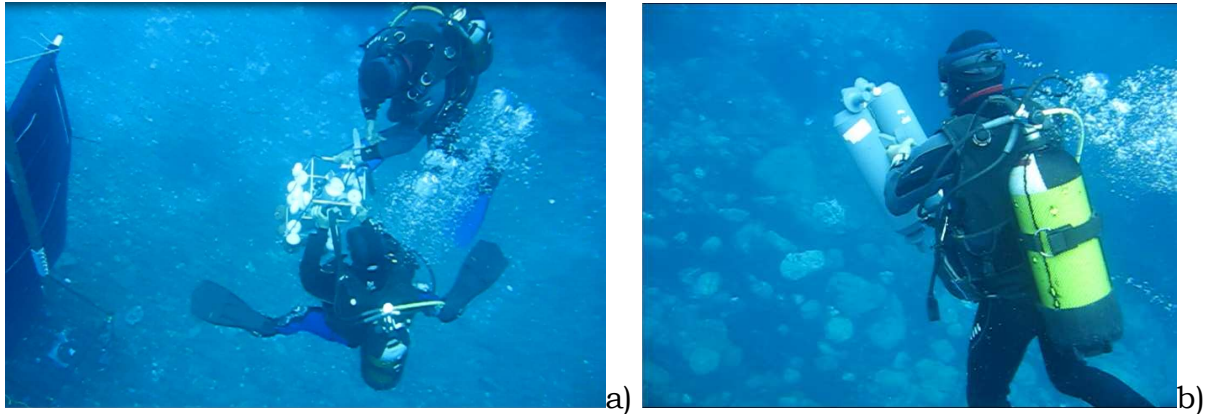


Figure 12. Divers carrying by hand the CTD probe to endure that the profile is conducted directly beside the video support structure.

## 5 SUMMARY

Work was performed at the Panarea natural laboratory by personnel from the Università di Roma La Sapienza and OGS during the period October 19 to 31, 2012 within the framework of Work Packages 2, 3, and 4 for the EC-funded research project ECO2. Research was divided into three main themes focussing on: i) chemical and biological processes in the sediments and along the water column; ii) the flux of gas bubbles and deep-origin brines from the sediments to the water column; and iii) the fate of gas bubbles within the water column.

Water sampling was conducted at the two stations close to Basiluzzo Island.

Sedimentary work was concentrated on two sites, one off the east coast of Basiluzzo Island and another just to the NE of Panarea Island itself. This work continued previous work done at the same sites during previous campaigns, but with an expanded list of analysed parameters and with the unique addition of primary and secondary production experiments. All planned measurements were successfully performed.

Flux measurements for gas bubbles were performed near Bottaro Island in the area known as the crater. Three areas were defined based on their average gas bubble flux

and 4 representative points were picketed in each area. All 12 points were measured on two different occasions to examine both spatial and temporal variability. This data will be used to make an overall estimate of the flux coming from the crater. Flux of dissolved CO<sub>2</sub>, carbonate system parameters, and dissolved elements were measured on two different occasions at a point to the NE of Panarea Island where high temperature indicate the leakage and flux of deep hydrothermal waters. Data from the pCO<sub>2</sub> probes showed an excellent response, as did the associated temperature sensor on the same probe. All gas and water flux measurements planned were successfully completed.

Finally a series of experiments were conducted to study gas bubble evolution during its ascent through the water column, with the hope of creating an all-encompassing dataset of many parameters that can be computer modelled. Work involved measuring bubble rise velocity, size, and composition at different heights above the sediments, as well as water chemistry parameters at discrete points (carbonate system parameters) and along the entire profile with a CTD (salinity and temperature). A total of three partial days were devoted to these experiments. The first two days involved testing various aspects of the experiment, whereas the third day was the only one where all planned measurements and samplings could be done. Unfortunately bad weather during the last two days prevented us from collecting more data after the success of the third day, however we are confident that the obtained results are of good quality and we have accumulated good experience which will help us during the next planned campaign.

## **6 ACKNOWLEDGEMENTS**

We thank Andrea Fogliuzzi and his assistant Ilaria Dalle Mura from the Amphibia Diving Center (Panarea, Italy) for their invaluable help in conducting these experiments.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 265847 (“Sub-seabed CO<sub>2</sub> Storage: Impact on Marine Ecosystems” – ECO2).

## **7 REFERENCES**

Beaubien S.E. and De Vittor C., 2012. Preliminary testing of an apparatus to study bubble behaviour in the water column off Panarea Island (Italy): Cruise Report ECO2-5 (2012). Università di Roma La Sapienza, Roma, Italy / Istituto Nazionale di Oceanografia e Geofisica Sperimentale, Trieste, Italy 17 pp.

Caliro S., Caracausi A., Chiodini G., Ditta M., Italiano F., Longo M., Minopoli C., Nuccio P.M., Paonita A. and Rizzo A., 2004. Evidence of a recent input of magmatic gases into the quiescent volcanic edifice of Panarea, Aeolian Islands, Italy. *Geophys. Res. Lett.*, 31(7): L07619.

Esposito A., Giordano G. and Anzidei M., 2006. The 2002-2003 submarine gas eruption at Panarea volcano (Aeolian Islands, Italy): Volcanology of the seafloor and implications for the hazard scenario. *Mar. Geol.*, 227(1-2): 119-134.

Tassi F., Capaccioni B., Caramanna G., Cinti D., Montegrossi G., Pizzino L., Quattrocchi F. and Vaselli O., 2009. Low-pH waters discharging from submarine vents at Panarea Island (Aeolian Islands, southern Italy) after the 2002 gas blast: Origin of hydrothermal fluids and implications for volcanic surveillance. *Appl. Geochem.*, 24(2): 246-254.