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Cover | In copertina Sicily map (by Barbara Angioni)

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Gases and seabed fluid fluxes at the Panarea shallow hydrothermal vents (Aeolian Islands)

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Introduction

CO_2 leaking into the shallow sediments and overlying seawater is partitioned in different forms, each migrating at its own rate and having potentially different impacts. To begin with the CO_2 gas will migrate through the shallow subsurface either alone as a free gas or together with associated deep fluids (e.g. brines), with the free-phase CO_2 equilibrating with the surrounding pore waters/associated brines. Migrating upward these fluids will enter the base of the water column, with the release of gas bubbles (and possibly associated waters) from the sediments into the overlying seawater. The bubbles will rise in the water column creating what is known as a bubble "flare" with the CO_2 in the bubbles dissolving in the surrounding surface water as they rise. Depending on the depth and the chemical/physical characteristics of the water column, these bubbles may or may not reach the water surface. Any co-migrating water/brine will also be released into the water column, creating a plume having a chemical composition that is distinct from the surrounding seawater, consisting of dissolved gases (mainly CO_2), elements in the original brine, and elements liberated via CO_2-induced water-rock interaction. The height that this dissolved plume will reach in the water column will depend on the original flow rate across the sediment-water interface and the density contrast between the plume and surrounding seawater. Both the gas-induced and water plumes will then migrate laterally and vertically as a result of the local currents, water column stratification, and density effects, meaning that there is the potential for impact both in the near and far field for pelagic organisms, both in terms of a lower pH and the possibility of elevated concentrations of toxic elements. This study was carried out in the framework of two EC funded projects, RISCS and ECO2 related to research on sub-seabed CO_2 storage as climate change mitigation strategy, and potential impact on marine ecosystems. Here, we investigated how CO_2-leakage, a risk associated with subseafloor CO_2-storage, can affect physical and chemical characteristics of the surrounding ecosystem. We studied the Panarea natural laboratory site (Aeolian Islands), where natural CO_2 is leaking from the seafloor into the overlying water column, as an analogue for a leakage scenario.

Study Area

Panarea (Figure 1a) is the smallest of the islands of the Aeolian archipelago (Tyrrhenian Sea, Italy) a 200 km long volcanic arc composed of 7 islands and 10 seamounts. It represents the emergent part of a wide stratovolcano that has been volcanically active over the last 400 ka. Deep origin magmatic CO_2 (and other trace gases) is released in large volumes to the east of Panarea Island into the overlying shallow marine environment near three small islets. This gas leaks along, or at the intersection between, two main gas-permeable fracture systems (NE-SW and NW-SE). Aside from occasional gas burst events linked to magma activity at great depth, the leaking gas is relatively stable in terms of both chemistry (e.g. 98% CO_2, 1.7% H_2S plus other trace gases) and flux rates (7-9 x 10^6

L d^{-1}) [Caliro et al., 2004]. The majority of emissions are of gas only, although at some points a mixture of geothermal water and seawater in different proportions is released.

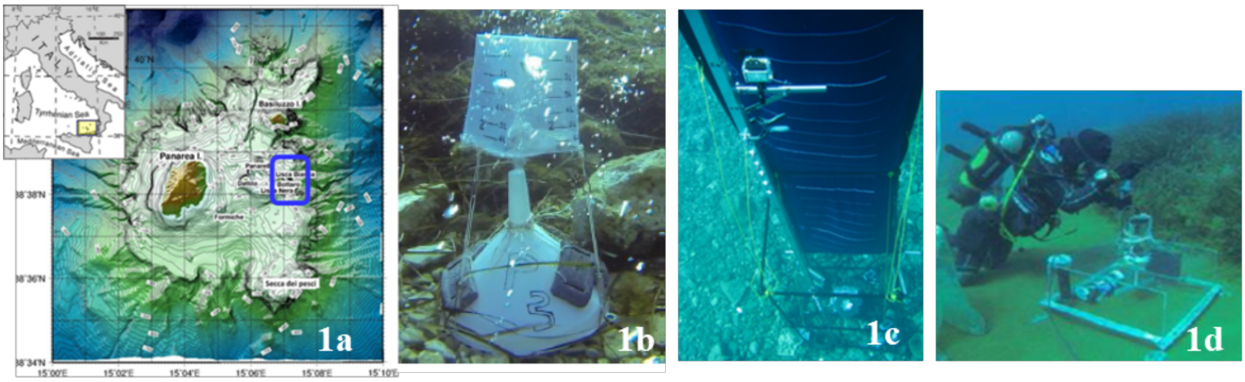


Figure 1 Study area (a), gas flux measurement (b), discrete bubble dynamics experiment (c), benthic flux measurement (d).

Experimental

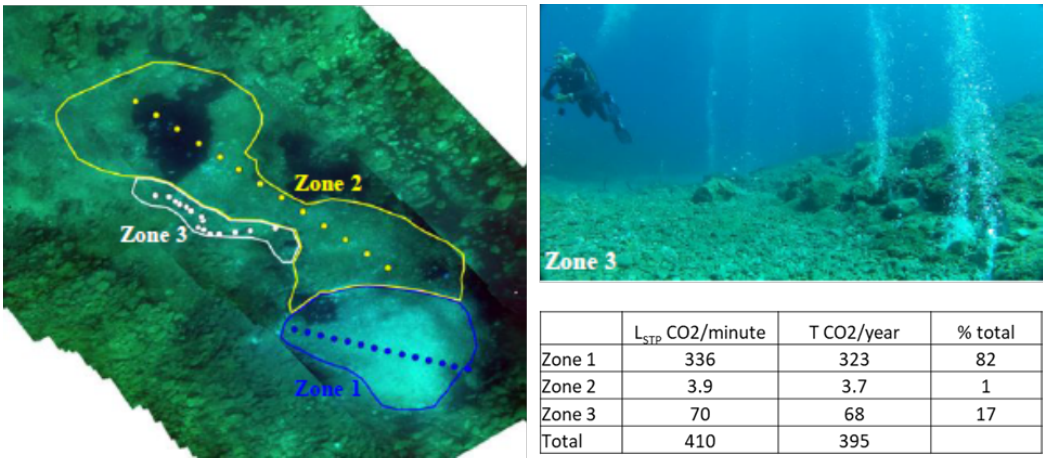
Different series of experiments were performed close to the Bottaro Islet (Figure 1a) where, on the 3rd of November 2002, an impressive “gas burst” (consisting of emissions of a mixture of gas mainly composed of CO_2, fine-grained suspended sediments and colloidal S released from the sea floor at a depth of 10-15 m) led to the formation of a crater-like depression about 20 x 14 m wide and 10 m deep [Tassi et al., 2009]. The aim was to measure gas fluxes and benthic fluxes and to model discrete bubbles dynamics in order to better understand the fate of CO_2 in the water column after it has migrated out of the sediments (Figure 1a-d).

Gas Bubble Fluxes

Gas fluxes from the sea floor to the overlying water column at the Bottaro Crater were measured in July 2014. Fluxes were calculated by measuring the time required to capture a given volume of gas (from 0.1 to 6 L) using a funnel of known surface area (0.17 m^2) and a graduated, inverted container (Figure 1b). Results were converted to STP (1 bar and 298.5 K) conditions to allow for a comparison of the volume flows at sites having different water depths, as well as a mass flux. The area of the Bottaro crater is in 8-10 m deep water, with the base of the crater itself at a depth of about 11-12 m. The crater was subdivided into three different zones (Figure 2) based on the different leakage styles present: Zone 1 is a semi-circular area of uniform diffuse degassing; Zone 2 has isolated points of weak leakage; and Zone 3 has isolated points of moderate to stronger leakage that form bubble flares.

Measurements in Zones 1 and 2 were conducted along linear, regularly spaced profiles, which were placed irrespective of leakage points to obtain a representative statistical estimate of the average leakage rate. Sample spacing was 1 m and 2 m, respectively, and the average flux for each profile was multiplied by that zone’s surface area to estimate total flow for that zone. In contrast, all major leakage points were measured in Zone 3 and all measured values were summed to calculate the total flux of this zone.

The zone and total flows estimated using the above described approach are summarized in the Table of Figure 2, which shows how most of the CO_2 leaking from the crater originates from the diffuse area of Zone 1 (c. 80%). It must be highlighted, however, that the assumptions made in extrapolating the individual point measurement results over the chosen surface area for that zone can influence the final calculated value. It is interesting to note, that whereas the diffuse degassing from Zone 1 is volumetrically the most important, the bubble flare from this feature does not rise as high in the water column as that observed for the individual points of Zone 3, some of which reached the water surface. This is due to the smaller average Zone 1 bubble size spread over a wider area, which allows for a more rapid dissolution. In contrast, the focussed flow from the moderate to strong individual vents results in larger bubbles that break-up and dissolve more slowly, which may allow for equilibration with O_2 and N_2 in the water column thus stabilizing and prolonging the “life” of the rising bubbles. This could have important consequences for hydroacoustic monitoring, and the use of this technique to estimate leakage rates for highly soluble gases like CO_2 (as opposed to less soluble ones like CH_4).



	L_{STP} CO2/minute	T CO2/year	% total
Zone 1	336	323	82
Zone 2	3.9	3.7	1
Zone 3	70	68	17
Total	410	395	

Figure 2 Montage of video stills taken from the water surface showing the Bottaro crater and the mapped zones with the associated table of estimates of CO_2 leakage rates given as both volume and mass flows.

Discrete Bubbles dynamics

As a CO_2 bubble rises it will exchange gases, such that CO_2 dissolves into the water and N_2 and O_2 are stripped out of the water into the bubble. These processes, combined with such factors as bubble diameter, 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_2 can then be transported via currents, react chemically or biologically, or can eventually be released to the atmosphere.

The bubble dynamic experiments were conducted primarily during a campaign in October 2012 and then repeated on May 2014, using a 3x1x1 m, hollow-tube frame, mounted on the floor of the Bottaro crater (12 m depth) in which natural CO_2 leakage is occurring. The structure had a 10 m tall guide mounted on the front face along which an HD video camera and other equipment can slide or be fixed and a dark blue cloth mounted on the back face (10 m tall) for contrast and distance from bottom measurements (Figure 1c). Bubbles were made using the gas released from the seafloor, but using a system which allowed for control of both bubble size and bubble numbers. The use of the *in situ* gas, within a leakage area that affects the surrounding water column, allowed us to conduct the experiment in real-world leakage scenario but with control on bubble characteristics. Measurements and sampling performed during the various experiments included: bubble rise velocity, bubble size at different heights, bubble composition at different heights, water column chemistry at different heights (carbonate system parameters and dissolved gases), and a CTD cast near the structure to obtain salinity, temperature, and DO profiles. In addition, two GasPro-pCO_2 sensors were deployed at different heights on the structure to continuously monitor dissolved CO_2 and temperature.

Bubble size decreased in an almost linear manner before disappearing at about 2 m above the release point. Bubble rise velocity averaged around 30 cm/s; the similar velocity despite changing bubble size implies the importance of the vertical current regime in influencing rise velocity in a natural system.

During the experiment, which lasted more than 3 hours, pCO_2 ranged from a minimum of 350 µatm to a maximum of 820 µatm. In collaboration with D. McGinnis (IGBB Berlin) these data have been modelled using the Discrete Bubble Model (DBM) [McGinnis et al., 2011]. Based on an input gas concentration equal to that of the first bubble measured, the model was able to predict very well the subsequent gas bubble concentrations measured higher in the water column. In contrast, a higher concentration was needed to match the bubble diameter values, perhaps indicating that the field technique for this measurement requires refinement.

Benthic fluxes

Benthic chambers (Fig 1d) were used to measure the flux of various chemical and biochemical components across the sediment water interface in October 2010, July 2011, January 2012 and March 2012. Two sites were measured in the Bottaro Crater, one near a point of gas leakage (referred to here as the "vent site") and a background site located about 100 m away where no leakage was observed (referred to here as the "control site"). Two different chambers were deployed at each site, one dark and one transparent. This was done to determine *in situ* benthic flux due to benthic metabolism (production and respiration) and diffusive fluxes from or into the sediments, as well as to assess the spatial variability of pore-water flux associated with the venting phenomena. Because the goal of these measurements was to study the flux of the aqueous phase and not the bubbles, the chambers deployed at the vent site were located near, but not on, the points of bubble emission. Sub-samples, collected from the benthic chambers by SCUBA divers with a plastic syringe approximately once every hour over a total deployment period of about 7 hours, were analysed for a wide range of parameters.

Of all the parameters measured during this study, only six show significant trends (in some or all chamber measurements) that are likely directly linked with a significant flux: dissolved inorganic carbon, pH, pCO_2, silica, hydrogen sulphide, and ammonium. At the control site, values are almost always low and stable throughout the measurement period. At the vent site, the first three campaigns show the most interesting results, illustrating slightly different behaviours. For example, examining the carbonate parameters, both in the transparent chamber of campaign 1 and in the opaque chamber of campaigns 3 a small increase in DIC (Dissolved Inorganic Carbon) was observed, however in the latter very large anomalies for both pH and pCO_2 where present, whereas in the former the anomalies are relatively small. In contrast, in both the opaque chambers of campaigns 2 and 3 large pH and pCO_2 anomalies were observed, but the DIC values of the latter are much smaller than those of the former.

Regarding benthic fluxes, most major elements showed relatively constant concentrations over the measurement period for both chambers at both sites, indicating little movement of these species out of the sediments into the overlying water column. Increased fluxes of the reduced gas H_2S were often observed at the vent site reaching the higher values during the second and third campaign (279992 and 263531 µmol $m^{-2}d^{-1}$, respectively). Among nutrients, a large flux of silica (18461 µmol $m^{-2}d^{-1}$) was measured at the vent site during the second campaign due to the co-migration of this nutrient with CO_2, as suggested by the significant correlation ($p<0.05$) between these two species; instead, all other deployments generally showed relatively low fluxes suggesting the overlapping of several processes such as microbial and chemical dissolution of opal, dependence on redox conditions, assimilation by benthic diatoms and flocculation and co-precipitation of silicon polymers and clay minerals with Fe(III).

Such differences can be attributed to spatial and / or temporal variability of pore water leakage, to diffusive versus advective flux modes, or to interference caused by the lateral ingress of denser, CO_2-charged bottom waters at the chamber base.

Conclusions

Work performed at the Panarea test site highlights the usefulness of studying natural leaking systems to obtain a more complete (and realistic) understanding of the possible consequences of a seabed leak of anthropogenic stored CO_2. Such large-scale, complex sites allow for a more assessment of the potential spatial and temporal impact of the leaking gas on marine chemistry, biology, and physics, as well as the testing of various parameters and new technologies for their sensitivity for leakage monitoring.

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